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KINETIC STUDIES OF SOME GROUP VI METAL CARBONYL COMPLEXES

by

James Richard Graham

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DOCTOR OF PHILOSOPHY

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1967

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEMES

INTRODUCTION

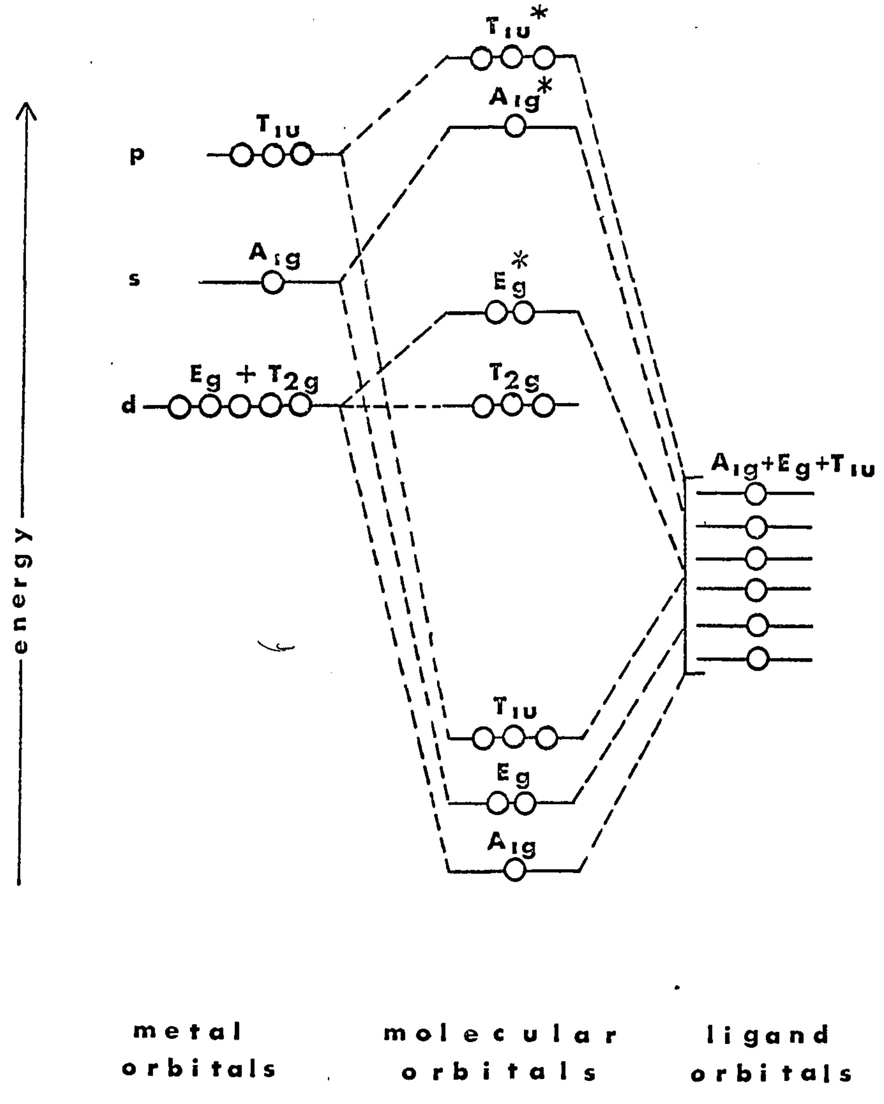
The bonding in octahedral transition metal complexes can be described in a number of ways. In the valence bond approach, the metal's d-orbitals can be hybridized with other orbitals on the metal (usually outer s and p-orbitals) to form new orbitals which are directed at the corners of an octahedron. These six hybrid orbitals on the metal can then form coordinate covalent bonds with the six ligands. This manner of explaining the bonding in transition metal complexes is of considerable interest since first of all it is fairly simple and offers a convenient way of talking about the bonding in these complexes, and secondly it offers a simple explanation to magnetic and other properties of these complexes (48).

Since carbon monoxide is an exceedingly weak Lewis base and does not form complexes with good Lewis acids such as BF_3 and $B(CH_3)_3$, it would not be expected to form stable complexes with transition metal Lewis acids if only coordinate covalent bonding (σ-bonding) were important (22). Valence bond theory explains the unexpected stability of metal carbonyl complexes by postulating resonance forms of the complexes which show considerable M-CO double bond character (48).

Molecular orbital theory however offers a much better approach (23, 8) to the bonding in transition metal complexes in general and to metal carbonyl complexes in particular. In the molecular orbital approach, MO's of the appropriate symmetry can be formulated on the metal by taking a linear combination of the metal's atomic orbitals. These orbitals can then overlap with ligand orbitals of the same symmetry and similar energy. The energy level diagram for the ligand and metal atomic orbitals and the resulting molecular orbitals for an octahedral complex are shown in Figure 1. From this diagram it can be seen that the σ-bonds are formed between the metal and the ligand by using the a_{1g}, t_{1u}, and the e_g orbitals. The t_{2g} orbitals on the metal, which are essentially the d_{xy}, d_{yz}, and d_{xz} atomic orbitals, are of the same symmetry as the anti-bonding p-orbitals on the carbonyl carbon, and therefore π-bonding can result from an overlap of these orbitals.

This concept of π-bonding in metal carbonyl complexes which comes out of both valence bond and molecular orbital theories very readily explains the unexpected stability of these complexes. It not only offers the explanation of how the expectedly weak M-CO σ-bond can be supplemented by M-CO π-bonding thus enhancing the stability of the complex, but it also offers a mechanism by which zero-valent transition metals can delocalize back out onto the carbonyl group the negative charge buildup which would result from the CO σ-bonds. When this d_π- p_π bonding occurs, electron density

Figure 1. Molecular orbital diagram for a typical octahedral complex


energy
p
T_{1u}
s
A_{1g}
d
$E_g + T_{2g}$
T_{1u}^*
A_{1g}^*
E_g^*
T_{2g}
T_{1u}
E_g
A_{1g}
$A_{1g}+E_g+T_{1u}$
metal orbitals
molecular orbitals
ligand orbitals

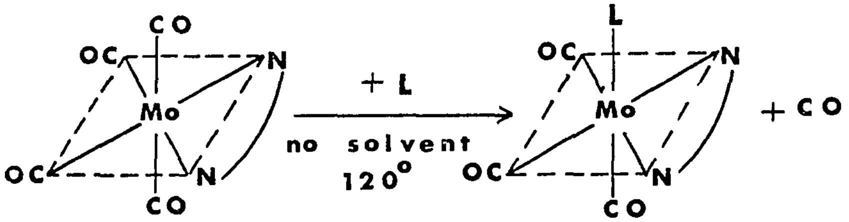
is donated from the d-orbitals on the metal into the anti-bonding p-orbitals on the carbonyl carbon. This has the effect of making the carbon atom more negative and thereby enhancing its electron donating ability and thus increasing the amount of M-C σ-bonding. Since in the carbonyl group the oxygen atom is slightly more electronegative than the carbon, some of the increased electron density resulting from the more negative carbon atom can be shifted out onto the oxygen atom. This would result in a lowering of the C-O bond order.

This particular point about the bonding in metal carbonyl complexes has been the topic of considerable recent interest by a number of workers (9, 25, 31, 52). The reason for this is that when a lowering in the C-O bond order is observed in metal carbonyl complexes there should be, if current π-bonding therories are correct, a corresponding increase in the amount of M-CO π-bonding.

A number of infrared studies on a large number of metal carbonyl complexes have indicated that this assumption is probably valid (46, 52). For example Poilblanc and Bigorgne have reported (52) an infrared study of some phosphine and phosphite derivatives of $Mo(CO)_6$. In their study they found that as the phosphine or phosphite was made more basic and the metal thereby correspondingly more negative, the M-C stretching frequencies increased and the C-O stretching frequencies decreased. This study indicates that the amount of M-C π-bonding is indeed increasing as the C-O bond order is decreasing.

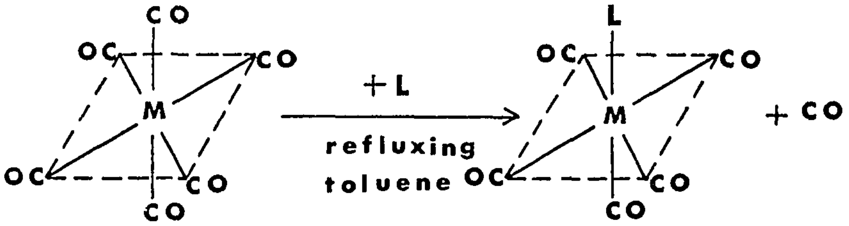
In transition metal complexes of octahedral symmetry there are only three orbitals of the proper symmetry available which can participate in π-bonding with the carbonyl groups. If the metal complex contains more than 3 CO groups, a complete π-bond to each CO group cannot be formed. Therefore, for example in the Group VI metal hexacarbonyls, the maximum possible amount of π-bonding to each CO group would be ½ of a π-bond (46). Each CO group would be in a sense "competing" with the other CO groups in the complex for electron density from the metal's d-orbitals. If one or more CO groups in the metal hexacarbonyls are replaced by a group which is not capable of participating in M-L π-bonding (such a group could be an amine), the result should be an increase in the amount of π-bonding to the remaining CO groups in the complex. Infrared studies indicate that this is probably true (40). For example Kraihanzel and Cotton found that upon subsequent replacement of CO groups in $Cr(CO)_6$ with pyridine, py, to form $Cr(CO)_5py$ and *cis*- $Cr(CO)_4(py)_2$ there was a corresponding lowering of the CO force constant (40). This indicates a decrease in the CO bond order and probably a corresponding increase in the amount of M-C π-bonding.

In 1963 Stiddard (55) carried out some preparative work under conditions which were milder than would have been predicted from current π-bonding theory. Stiddard reacted $Mo(CO)_4(dipy)$ with ligands such as pyridine, triphenyl phosphine and diphenyl sulfide according to Equation 1 under conditionswhich are similar to those nec-



(1)

essary to react $Mo(CO)_6$ with similar ligands (Equation 2)



(2)

(6, 65, 66, 67). This preparation was surprising to us because the replacement of two CO groups in $Mo(CO)_6$ by a dipyridyl ligand which would be at best a very poor π-bonder to form $Mo(CO)_4(dipy)$ should presumably, if the current π-bonding arguments are correct, increase the molybdenum π-bonding to the remaining four C-O groups thus rendering them more inert than those in $Mo(CO)_6$. Since the preparative work by Stiddard indicated that the CO groups in $Mo(CO)_4$(dipy) were probably more labile than the CO groups in $Mo(CO)_6$, a preliminary kinetic study was conducted to see if this was true. The first results indicated that indeed the CO groups in $Mo(CO)_4$(dipy) were substantially labilized as compared to the metal hexacarbonyls.

Since $Mo(CO)_4$(dipy) seemed to be a complex which was much more reactive than would be predicted from the current bonding theories for metal carbonyl complexes, a thorough kinetic, infrared, and equilibrium study was carried on this complex and similar complexes for the other Group VI metals. These studies were undertaken in an attempt to learn why this unexpected labilization was taking place and to see if the answer was indeed inconsistent with current π-bonding theories.

EXPERIMENTAL

Purification of Solvents and Ligands

Decalin was purified by first refluxing over sodium metal for several hours and then fractionally distilling at reduced pressures. The solvents, 1,2-dichloroethane and o-dichlorobenzene, were purified by fractional distillation. Chlorobenzene and nitrobenzene were first dried over P_4O_{10} before being fractionally distilled, while reagent grade acetone was used without any prior purification. All of the purified solvents were stored in 1-liter round-bottom flasks equipped with stopcocks so that the solvents could always be kept under a nitrogen atmosphere.

The bicyclic ligands, 4-methyl-3,6,7,-trioxa-1-phosphabicyclo [2.2.2] octane, $P(OCH_2)_3CCH_3$, and 1-phospha-2,8,9-trioxaadamantane, $PO_3C_6H_9$, were obtained by refluxing $P(OCH_3)_3$ with the appropriate triol (63). Trimethyl phosphite, $P(OCH_3)_3$, (Eastman Chemicals), triethyl phosphite, $P(OC_2H_5)_3$, tributyl phosphite, $P(O\text{-}\underline{n}\text{-}C_4H_9)_3$, (Matheson, Coleman, and Bell), and tri-n-butyl phosphine, $P(\underline{n}\text{-}C_4H_9)_3$, (Aldrich Chemical Co.) were purified by fractional distillation at reduced pressures. Triphenyl phosphine, $P(C_6H_5)_3$, triphenyl phosphite, $P(OC_6H_5)_3$, and triphenyl arsine, $As(C_6H_5)_3$, (Eastman Chemicals) were used as obtained. The ligand, tri-iso-propyl phosphite, $P(OCH(CH_3)_2)_3$, was prepared by slowly adding with rapid stirring and slight cooling a hexane solution of PCl_3 to a hexane solution containing iso-propyl alcohol and N,N'-dimethylaniline as the tertiary base. After completion of the reaction the N,N'-dimethylaniline hydrochloride was filtered off and the product isolated by distilling in vacuum (39). The phosphite was identified from its N.M.R. spectrum which consisted essentially of a fairly well defined 14 line multiplet at about 4.5 p.p.m. which corresponded to the single methine hydrogen and a triplet at 1.25 p.p.m. for the methyl hydrogens. Tricyclohexyl phosphine, $P(C_6H_{11})_3$, was prepared and purified by the method described by Issleib (36).

Preparation and Purification of Reactants

The Group VI metal hexacarbonyls were very readily purified by subliming under vacuum (~0.1 mm of Hg) at between 40 and 60°C. The $Cr(CO)_6$ was purchased from the Pressure Chemical Company while $Mo(CO)_6$ and $W(CO)_6$ were received as gifts from the Climax Molybdenum Company.

Complexes of the type $M(CO)_4(N\text{-}N)$, where M = Cr, Mo, and W and N-N = 2,2'-dipridyl and 4,4'-dimethyl-2,2'-dipyridyl, were prepared from the metal hexacarbonyl and the desired dipyridyl as described in the literature (55) and identified by their infrared spectra (40).

$Mo(CO)_4$(1,2-diamino-2-methylpropane) was prepared by refluxing 0.65 g. of $Mo(CO)_6$ and 1 ml. of 1,2-diamino-2-methylpropane in 10 ml. of toluene for 30 minutes. The reaction solution was allowed to cool to room temperature and pentane was added. Upon cooling in an ice-water bath, a good yield of the desired light yellow compound was obtained. The complex was purified by recrystallizing 3 times from dichloromethane at -80°.

Anal. Calcd. for $Mo(CO)_4$(1,2-diamino-2-methylpropane): C, 32.5; H, 4.06. Found: C, 32.7; H, 3.93.

The analogous 1,2-diamino-2-methylpropane complex of Cr was prepared in about 20% yield by ultraviolet irradiation for 8 hours of a solution composed of 20 ml. tetrahydrofuran which had been dried by distilling from Na, 0.60 g. $Cr(CO)_6$, and 1 ml. of freshly distilled 1,2-diamino-2-methylpropane. The product precipitated upon treatment of the solution with water. The yield was found to be very sensitive to traces of impurities in the reagents and to traces of air. The complex was purified by recrystallizing from toluene at Dry-Ice temperatures and identified by comparing its C-O stretching spectrum with that of the analogous Mo complex.

The substituted o-phenathroline complexes, $M(CO)_4$(X-o-phen), were prepared by refluxing 1:1 molar ratios of the metal hexacarbonyl and X-o-phen* in toluene (when M was Cr

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*The substituted o-phenanthrolines were received as gifts from Professor H. Diehl.

or Mo) or xylene (when M was W). These preparations, which are analogous to those reported for the dipyridyl complexes (55), were found to be satisfactory only when electron withdrawing groups (5-nitro, 5,6-dichloro, and 4,7-diphenyl) were not present in the o-phenanthroline.

Anal. Calcd. for $Mo(CO)_4(3\text{-}CH_3\text{-}o\text{-}phen)$: C, 50.7; H, 2.49. Found: C, 50.5; H, 2.30.

Anal. Calcd. for $Mo(CO)_4$(3,4,7,8-tetramethyl-o-phen): C, 54.1; H, 3.60. Found: C, 54.1; H, 4.09.

The other $M(CO)_4$(X-o-phen) complexes were identified from their infrared spectra in the C-O stretching region (Table 17).

Complexes of the o-phenanthrolines substituted by 5-nitro, 5,6-dichloro, and 4,7-diphenyl were prepared by the ultraviolet irradiation of an acetone solution containing a 1:1 molar ratio of the appropriate metal hexacarbonyl and substituted o-phenanthroline. The irradiations were carried out under a nitrogen atmosphere for a period of between 4 and 6 hours. The complexes were isolated from the acetone solutions by evaporating the solvent at reduced pressure and purified by recrystallizing the crude product from dichloromethane at -80°.

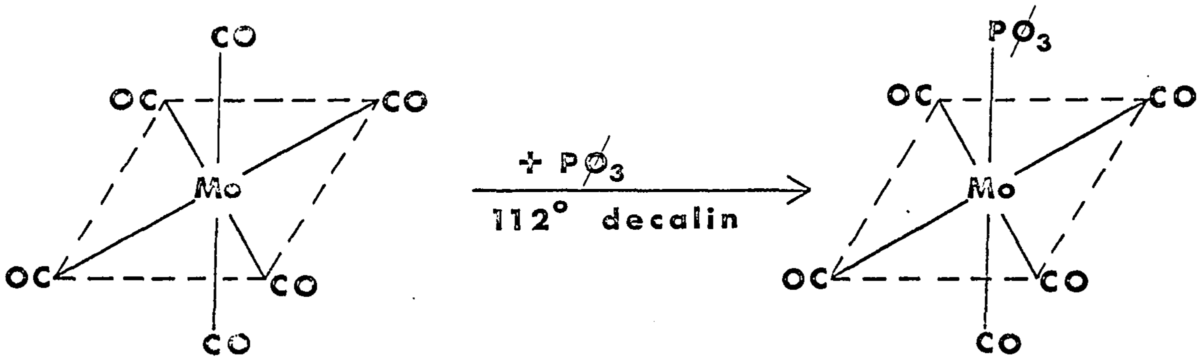
$Cr(CO)_5py$ and $Mo(CO)_5py$, where py = pyridine, were prepared and purified by the method outlined by Strohmeier and Gerlach (56). They were identified by their infrared spectra (40).

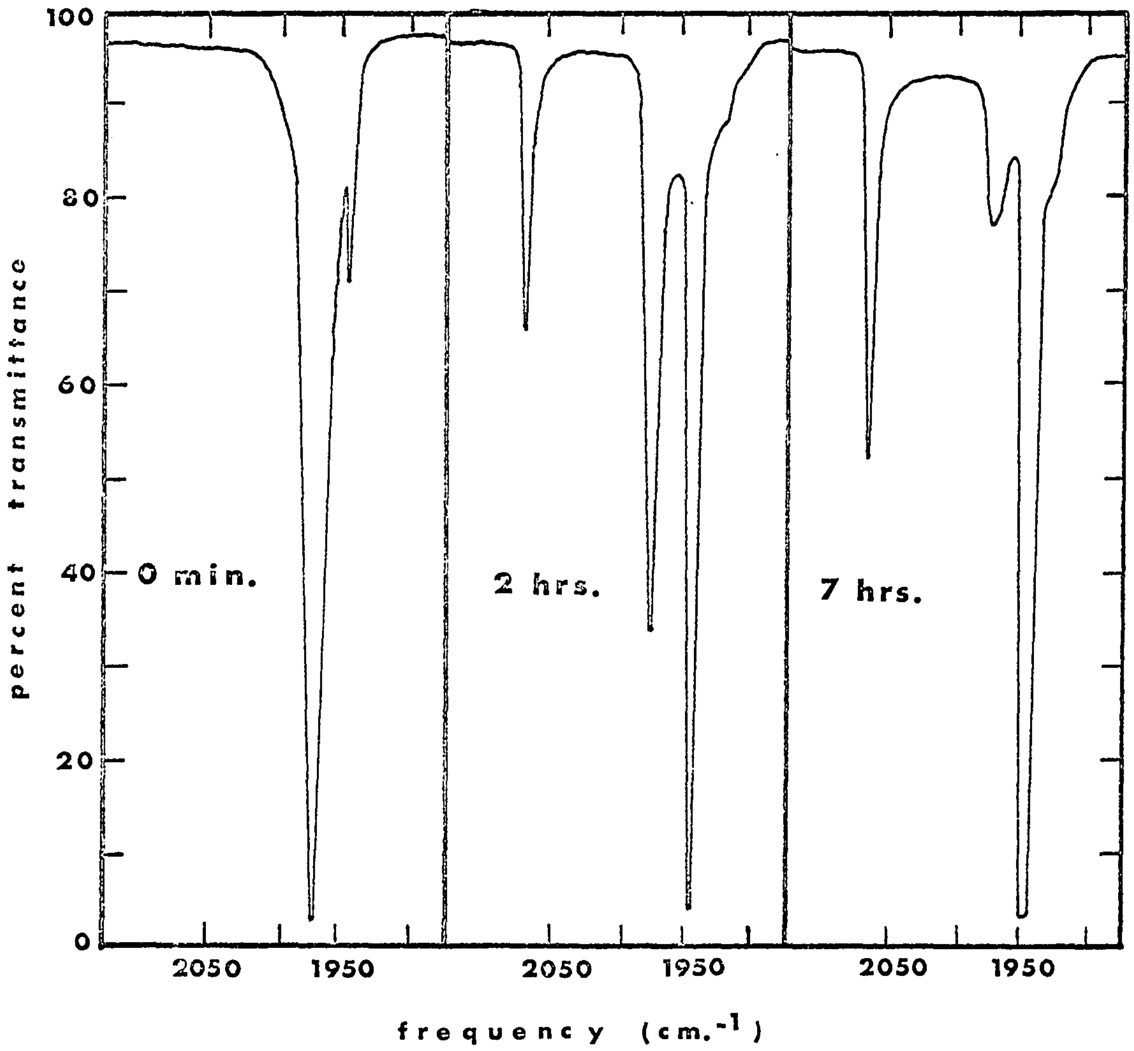
Determination of Reaction Rates and Reaction Products

Hexacarbonyls of Group VI

The infrared spectrum of $M(CO)_6$, where M = Cr, Mo, or W, in the C-O stretching region consists essentially of one very intense absorption at about 1980 $cm.^{-1}$. When $M(CO)_6$ reacts with phosphines and phosphites according to Equation 2, this strong C-O absorption begins to disappear and is replaced by the two C-O absorptions of the reaction product, $M(CO)_5L$. Since there is no overlap of the product bands with the stretching absorption of the hexacarbonyl (Figure 2), the rates of reaction were determined by following the disappearance of the $M(CO)_6$ band with time. The concentration of L for a particular run was essentially constant because its concentration was always greater than 15 times the concentration of $M(CO)_6$. Linear plots of $\ln(A - A\infty)$, where A is the absorbance at any time and $A\infty$ is the absorbance at infinite time, versus time, t, had slopes which were the pseudo-first order rate constants, $k_{obsd.}$, for the reaction. The plots of $\ln(A - A\infty)$ vs. t were linear to at least 80% reaction completion, and the average deviation of the rate constants for identical runs was normally less than 3% for the $Cr(CO)_6$ and $Mo(CO)_6$ reactions and less than 5% for the

Figure 2. Infrared spectra for the reaction of $Mo(CO)_6$ with triphenyl phosphine in decalin at 112°


CO
OC
CO
Mo
OC
CO
CO
+ PØ3
112° decalin
PØ3
OC
CO
Mo
OC
CO
CO

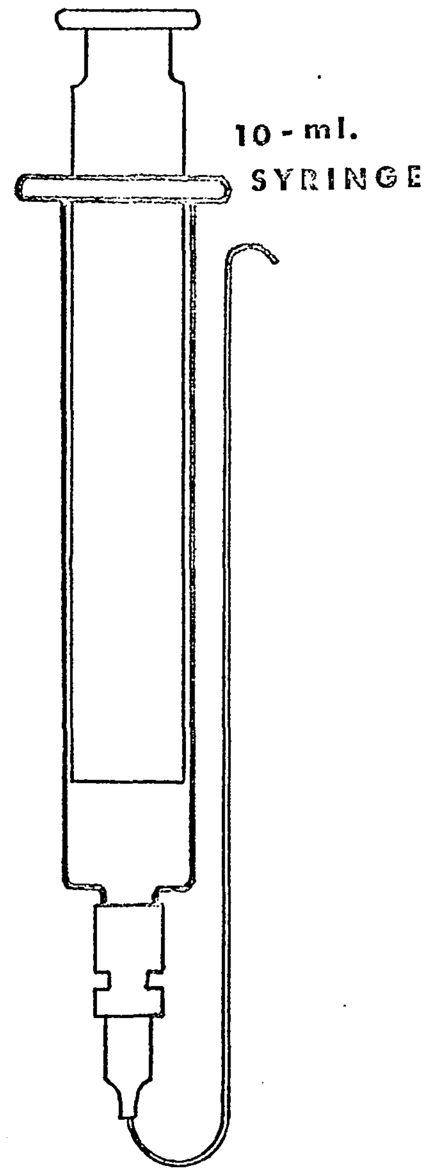

100
80
60
40
20
0
percent transmittance
0 min.
2 hrs.
7 hrs.
2050
1950
2050
1950
2050
1950
frequency (cm.-1)

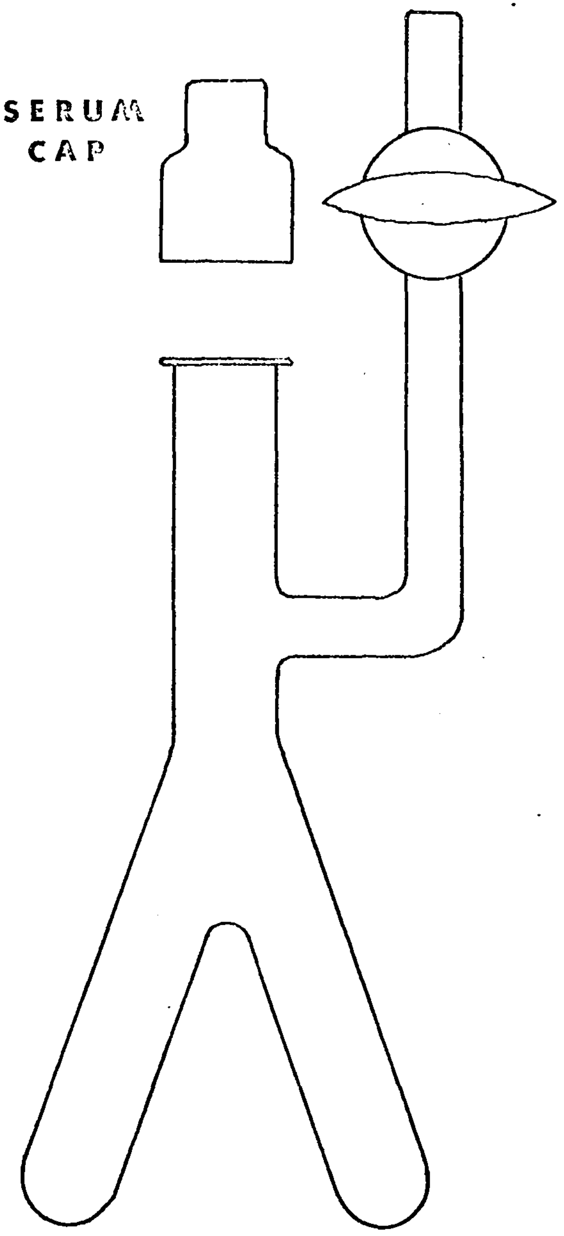
$W(CO)_6$ reactions.

The reaction rates were determined on a Beckman IR-8 infrared spectrophotometer using NaCl cells with 0.5 mm. spacers. Since the reaction of $M(CO)_6$ with L proceeds only at relatively high temperatures (>100°C) a constant temperature oil bath (±0.05°) was used to thermally equilibrate the reaction vessels. At these temperatures the Group VI metal hexacarbonyls are quite volatile and had a tendency to sublime from the reaction solution. To eliminate this problem during a kinetic run, a reaction vessel (Figure 3) was used that eliminated any gas phase above the reaction solution. It consisted of a 10 ml. syringe equipped with a long syringe needle that was bent in such a manner as to allow samples to be removed from the syringe while it was partially submerged in the constant temperature oil bath. Although CO gas is one product of the reaction, it caused no problems about forming a gas phase in the reaction vessel because the small amounts liberated were completely soluble in the solvent.

A typical kinetic run was carried out in the following manner. The ligand, L, and the $M(CO)_6$ were weighed out in a 10 ml. volumetric flask and then diluted to 10 ml. with decalin. The amount of $M(CO)_6$ used depended upon the reaction temperature. Enough $M(CO)_6$ (between 6×10^{-4} and 12×10^{-4} M) was added to each run so as to allow the reaction solution to be thermally equilibrated in the oil

Figure 3. Reaction vessels used in the kinetic studies


10-ml.
SYRINGE


SERUM
CAP

bath for between 20 to 30 minutes and still have sufficient hexacarbonyl remaining to give an absorbance of at least 0.8. The syringes were filled with the reaction solutions in a nitrogen filled glove bag thus assuring that the kinetic measurements were carried out under a nitrogen atmosphere. After the equilibration time, the absorbance of the reaction solution was measured at 5 to 15 minute time intervals.

The product of the reaction of $M(CO)_6$ with L is $M(CO)_5L$. For the poorer nucleophiles such as $P(C_6H_5)_3$, $P(OC_6H_5)_3$, and $As(C_6H_5)_3$ this was the only product observed to be formed at the reaction temperatures studied. For $P(\underline{n}\text{-}C_4H_9)_3$, a good nucleophilic reagent, a small amount of $M(CO)_4[P(\underline{n}\text{-}C_4H_9)]_2$ was formed at the higher temperatures studied. It resulted from the reaction of $M(CO)_5[P(\underline{n}\text{-}C_4H_9)_3]$ with excess ligand. Most of the complexes of the type $M(CO)_5L$ formed in this study had been prepared before and their infrared spectra are reported in the literature (52). This provided a convenient method of identifying the reaction products.

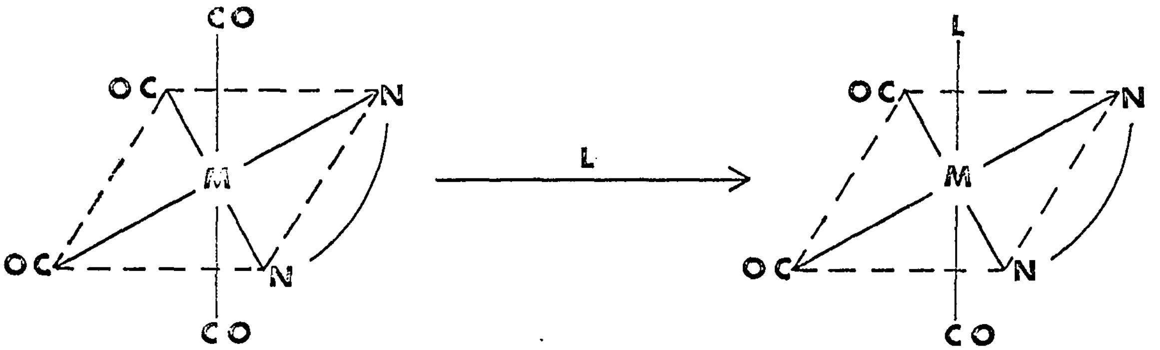
Complexes of the type $M(CO)_4(N\text{-}N)$

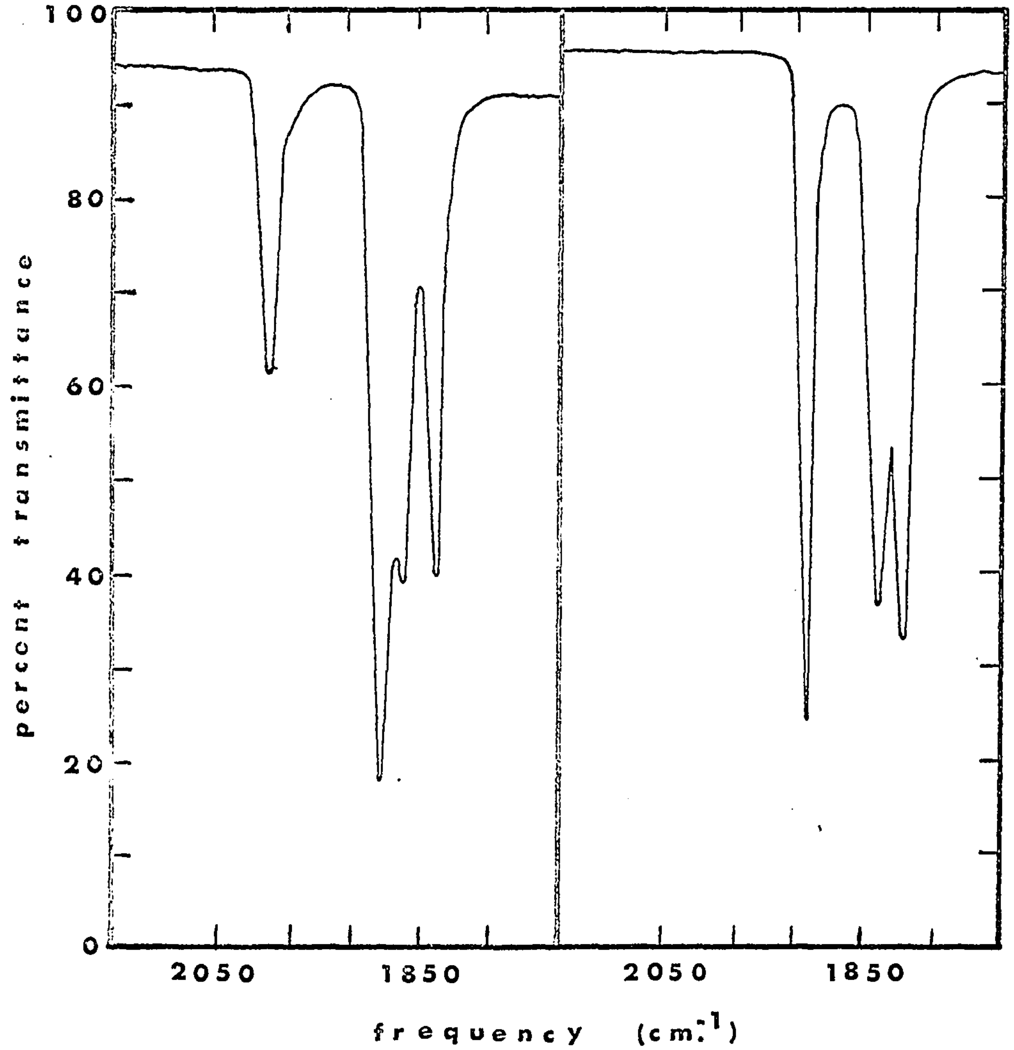
All of the complexes of the type $M(CO)_4(N\text{-}N)$, where M = Cr, Mo, and W and N-N = 2,2'-dipyridyl, 4,4'-dimethyl-2,2'-dipyridyl, X-o-phen, and 1,2-diamino-2-methylpropane, used in this study have infrared spectra that show C-O stretching absorptions at approximately 2010 M, 1900 VS, 1880 S, and 1830 S cm.$^{-1}$, the exact frequencies being dependent on the metal and the nature of N-N. When $M(CO)_4(N-N)$ reacts with a ligand, L, its four C-O stretching absorptions are replaced by the absorptions of the products. Since none of the reaction product bands interfere with the C-O absorption of $M(CO)_4(N-N)$ at about 2010 cm.$^{-1}$, its rate of disappearance with time was used to determine the rate of reaction. Linear plots of $\ln(A - A\infty)$ vs. time yielded $k_{obsd.}$, the pseudo-first order rate constant.

The kinetic studies were carried out in a two-compartment reaction vessel (Figure 3) which was fitted with a side-arm stopcock to allow the reaction mixture to be maintained under a nitrogen atmosphere. The top of the vessel was sealed with a serum cap. At the beginning of a run a solution of the complex was pipetted into one compartment of the vessel and the ligand solution pipetted into the other. These solutions were allowed to thermally equilibrate in a constant temperature bath for about 30 minutes before the reactant solutions were thoroughly mixed by tilting the vessel. Absorbance readings at about 2010 cm.$^{-1}$ were made on the solution by withdrawing samples at appropriate time intervals. Concentrations of the $M(CO)_4(N-N)$ complexes were approximately 5×10^{-3} M.

Average deviations for the rate constants, $k_{obsd.}$, were usually less than 3%. A general non-linear least squares

Figure 4. Infrared spectra taken before and after the reaction of $M(CO)_4(N-N)$ with L. These spectra were taken in 1,2-dichloroethane


CO
OC
N
M
OC
N
CO
L
L
OC
N
M
OC
N
CO


100
80
60
40
20
0
percent transmittance
2050
1850
2050
1850
frequency (cm.$^{-1}$)

computer program (43) was used to calculate the values of the activation parameters and their standard deviations listed in Table 5.

The reactions of $M(CO)_4(N\text{-}N)$ with L can be divided into two types with regard to the reaction products formed. The first type contains the reactions which yield cis-$M(CO)_3(N\text{-}N)L$ as the only metal carbonyl product (Equation 8). All of the $Cr(CO)_4(N\text{-}N)$ and $M(CO)_4$(X-o-phen) complexes belong to this class. The other $M(CO)_4(N\text{-}N)$ complexes yield not only cis-$M(CO)_3(N\text{-}N)L$ as a reaction product but also some cis-$M(CO)_4L_2$ and cis-$M(CO)_3L_3$ (Equation 6).

In order to confirm the identity of the products of the reaction of $M(CO)_4(N\text{-}N)$ with L, most were prepared on a preparative scale, analyzed, and then the infrared spectra of the isolated products were compared with the infrared spectra obtained after the reactions of $M(CO)_4(N\text{-}N)$ with L.

To confirm the identity of the product of the reaction of $Cr(CO)_4$(dipy) with $P(OCH_2)_3CCH_3$, 0.64 g. of $Cr(CO)_4$(dipy) and 0.50 g. of $P(OCH_2)_3CCH_3$ were allowed to react in 10 ml. of refluxing 1,2-dichloroethane under a nitrogen atmosphere for about 1.5 hours. Cooling the 1,2-dichloroethane solution in a Dry Ice-acetone bath resulted in the separation of black product crystals. After rinsing several times with hexane, the crystals were dried under vacuum for several hours.

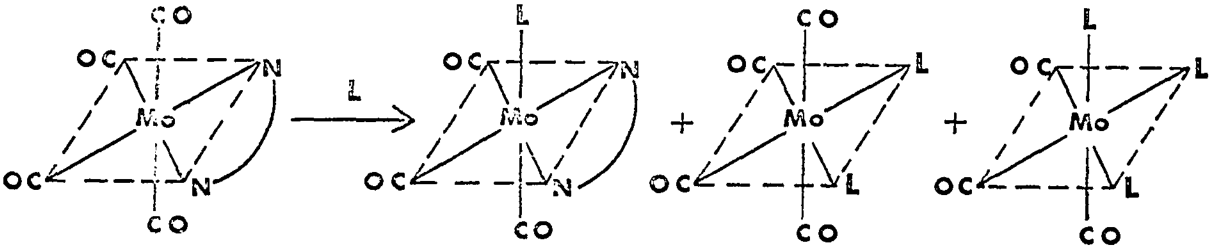
Anal. Calcd. for $Cr(CO)_3[P(OCH_2)_3CCH_3](dipy)$: C, 49.1; H, 3.86. Found: C, 49.0; H, 3.85.

This compound had an infrared spectrum that was identical with those obtained in the kinetic studies and was the only product of the reaction. With other ligands such as $P(OC_2H_5)_3$ and $PO_3C_6H_9$, the product absorptions were virtually identical with those noted above. It was therefore assumed that these ligands formed analogous compounds. The reaction of $Cr(CO)_4$(4,4'-dimethyldipy) with $P(OCH_2)_3CCH_3$ also showed the expected spectrum, which was taken to be positive identification for $Cr(CO)_3$(4,4'-dimethyldipy)L.

Because of the transparency of the solvents in the C-O stretching region of the spectrum, identification of the reaction product was easily noted in 1,2-dichloroethane, acetone, and chloroform; but in chlorobenzene and nitrobenzene, solvent absorptions obscured the product bands, and it was necessary to assume that the same product was also obtained in these solvents. This was supported by the fact that the expected maroon to purple color change also occurred in these solvents during the course of the reaction.

The infrared spectrum obtained after the reaction of $Mo(CO)_4$(dipy) with $P(OCH_2)_3CCH_3$ in 1,2-dichloroethane had gone to completion consisted of five bands (Figure 5). The presence of cis-$Mo(CO)_3[P(OCH_2)_3CCH_3](dipy)$ as a product was immediately evident from the three bands at 1938, 1835, and

Figure 5. Infrared spectra: (A) $Mo(CO)_4(dipy)$; (B) and (C) products of the reaction of $Mo(CO)_4(dipy)$ with 0.717 and 0.047 M $P(OCH_2)_3CCH_3$, respectively, in 1,2-dichloroethane


CO
OC
N
Mo
OC
N
CO
L
L
OC
Mo
N
OC
N
CO
+
CO
OC
L
Mo
OC
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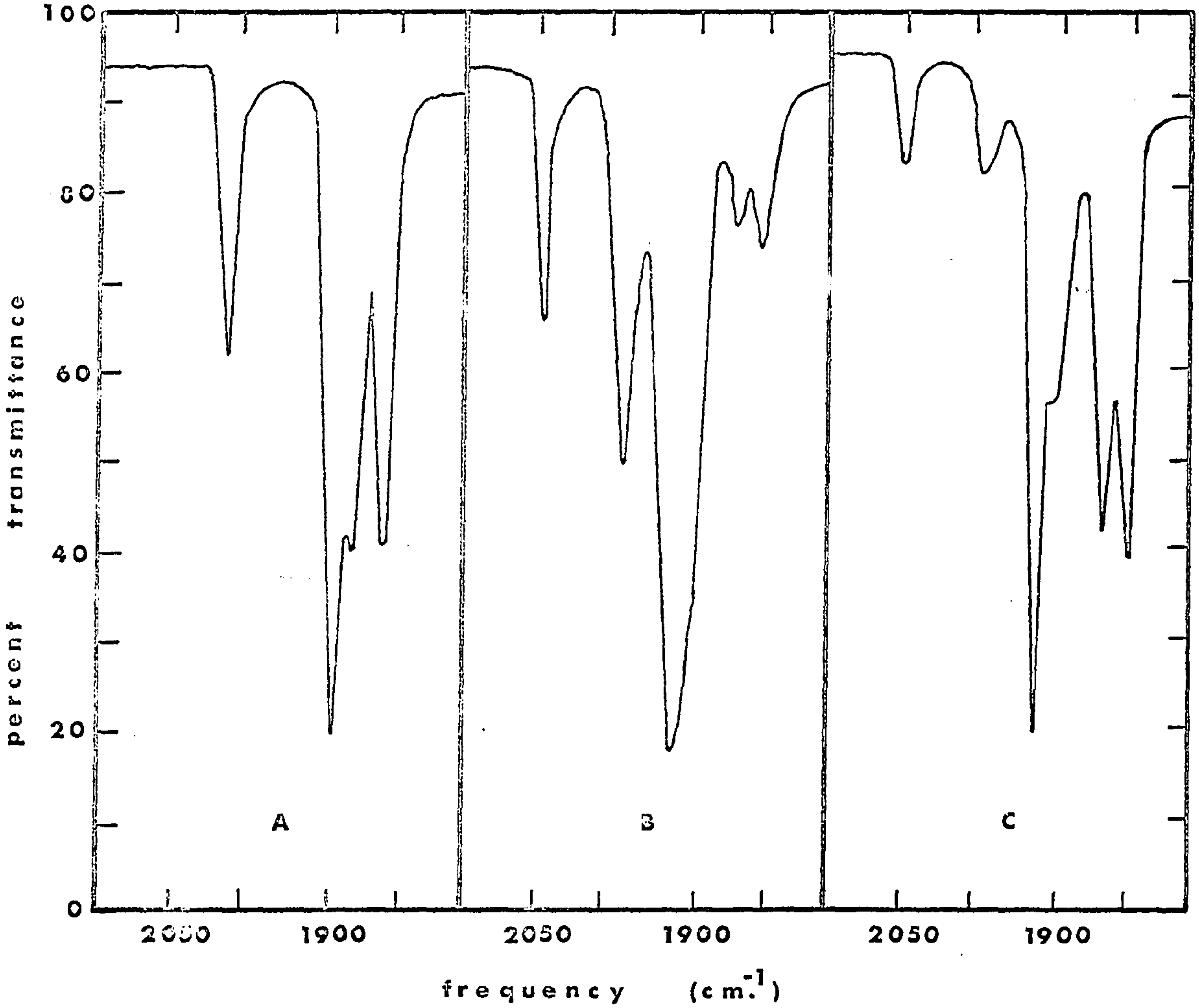
OC
L
Mo
OC
L
CO


100
80
60
40
20
0
percent transmittance
A
B
C
2050
1900
2050
1900
2050
1900
frequency (cm.⁻¹)

1790 cm.$^{-1}$, which are almost identical in position and intensity to those of $Cr(CO)_3[P(OCH_2)_3CCH_3](dipy)$. The bands at 2050, 2000, and 1930 cm.$^{-1}$ correspond quite well to the compound _cis_-$Mo(CO)_4[P(OCH_2)_3CCH_3]_2$ (63), and the bands at 1998 and 1930 cm.$^{-1}$ indicated the presence of _cis_-$Mo(CO)_3[P(OCH_2)_3CCH_3]_3$ in the reaction mixture.

Since during the kinetic runs a large excess of the ligand was used, the isolation of pure reaction products from the reaction mixtures was inconvenient. These products were therefore prepared in larger quantities as follows: $Mo(CO)_3[P(OCH_2)_3CCH_3](dipy)$ was obtained by refluxing under nitrogen in 10 ml. of 1,2-dichloroethane for about 1.5 hr. 0.72 g. of $Mo(CO)_4(dipy)$ and 0.35 g. of $P(OCH_2)_3CCH_3$. A reddish black solid precipitated from the solution upon cooling to room temperature. This material was filtered, washed thoroughly with pentane, and dried under high vacuum. A yield of greater than 90% was obtained.

Anal. Calcd. for $Mo(CO)_3[P(OCH_2)_3CCH_3](dipy)$: C, 44.8; H, 3.54. Found: C, 44.9; H, 3.98.

The other products of the reaction were prepared by refluxing in 20 ml. of 1,2-dichloroethane for 12 hr. 1.1 g. of $Mo(CO)_4(dipy)$ and a five fold excess (2.5 g.) of $P(OCH_2)_3CCH_3$. Upon cooling the reaction mixture to room temperature, a white crystalline solid was separated. The white crystals were washed thoroughly with pentane and dried under vacuum.

Anal. Calcd. for $Mo(CO)_3[P(OCH_2)_3CCH_3]_3$: C, 34.1; H, 4.26. Found: C, 34.1; H, 4.38.

To the filtrate from the above reaction was added an equal volume of pentane. A white powder was obtained. This powder was recrystallized several times by dissolving the substance in hot acetone and precipitating with water.

Anal. Calcd. for $Mo(CO)_4[P(OCH_2)_3CCH_3]_2$: C, 34.6; H, 4.33. Found: C, 35.1; H, 4.02.

Because of the high temperature required for the $W(CO)_4$(dipy) reactions, $W(CO)_4$(dipy) was allowed to react with phosphites in chlorobenzene. In this solvent C-O absorptions below 2000 cm.$^{-1}$ are obscured by absorptions due to the solvent. Therefore the products of the $W(CO)_4$(dipy) reactions were isolated from the chlorobenzene by precipitation with pentane. The infrared spectra of the products were then run in 1,2-dichloroethane. Except for the expected slight shift in frequencies, they were identical with the spectra obtained for the reactions of $Mo(CO)_4$ (dipy) with L. It was therefore concluded that analogous products, that is, cis-$W(CO)_3$(L)(dipy), cis-$W(CO)_4L_2$, and cis-$W(CO)_3L_3$ were also formed in these reactions.

The reaction products for the reaction of $M(CO)_4$(X-o-phen) with L were usually identified by their infrared spectra. However in one case it was isolated on a preparative scale and analyzed. A 1,2-dichloroethane solution of 0.80 g. $Mo(CO)_4$(3,4,7,8-tetramethyl-*o*-phen) and 0.70 g. $P(OCH_2)_3CCH_3$ was refluxed for 1 hr. under nitrogen. After cooling to room temperature and filtering, the product was precipitated with hexane. It was washed several times with hexane and dried under vacuum.

Anal. Calcd. for $Mo(CO)_3[P(OCH_2)_3CCH_3]$(3,4,7,8-tetramethyl-*o*-phen): C, 51.1; H, 4.43. Found: C, 51.0; H, 4.54.

The infrared spectrum (Table 17) of this compound was identical to that observed at infinite time for the reaction between $Mo(CO)_4$(3,4,7,8-tetramethyl-*o*-phen) and $P(OCH_2)_3CCH_3$. All of the $M(CO)_4$(X-*o*-phen) complexes reacted with L to form products, $M(CO)_3$(L)(X-*o*-phen), having very similar spectra.

During the reaction of $Mo(CO)_4$(1,2-diamino-2-methylpropane) with $P(OCH_2)_3CCH_3$ three products are formed. Two of the products, *cis*-$Mo(CO)_4[P(OCH_2)_3CCH_3]_2$ and *cis*-$Mo(CO)_3[P(OCH_2)_3CCH_3]_3$ were observed and identified in the reaction of $Mo(CO)_4$(dipy) with $P(OCH_2)_3CCH_3$. Their identity here was established on the basis of their C-O stretching spectra. The third product, *cis*-$Mo(CO)_3[P(OCH_2)_3CCH_3]$(1,2-diamino-2-methylpropane), was identified from a comparison of the reaction product spectrum with the spectrum of the compound prepared in the following manner: 0.63 g. of $Mo(CO)_4$(1,2-diamino-2-methylpropane) and 0.35 g. of $P(OCH_2)_3CCH_3$ were refluxed in 1,2-dichloroethane for 1.5 hrs. Upon slowly cooling to room temperature light brown crystals separated. After filtering, the crystals were washed with pentane and dried, then washed with water, 6N HCl, water and 20 ml. acetone. It was finally dried under vacuum.

Anal. Calcd. for $Mo(CO)_3[P(OCH_2)_3CCH_3]$(1,2-diamino-2-methylpropane): C, 34.6; H, 5.06. Found: C, 34.8; H, 5.44.

The analogous reaction of $Cr(CO)_4$(1,2-diamino-2-methylpropane) with $P(OCH_2)_3CCH_3$ yielded only $Cr(CO)_3[P(OCH_2)_3CCH_3]$ (1,2-diamino-2-methylpropane) as identified from its infrared spectrum which was essentially identical to that of the previously characterized $Mo(CO)_3[P(OCH_2)_3CCH_3]$(1,2-diamino-2-methylpropane). If $Cr(CO)_3[P(OCH_2)_3CCH_3]$(1,2-diamino-2-methylpropane) is allowed to remain in the presence of excess $P(OCH_2)_3CCH_3$, the chelate ligand is slowly displaced to give cis-$Cr(CO)_3[P(OCH_2)_3CCH_3]_3$.

Infrared spectra

All of the kinetic measurements were made on a Beckman IR-8 infrared spectrophotometer. Infrared frequency measurements as in Table 17 were made on a Beckman IR-9 and are estimated to be accurate to ±1 cm.$^{-1}$ but reproducible to ±0.5 cm.$^{-1}$. For the data in Table 17 NaCl cells equipped with 0.5 mm. spacers were used and $CHCl_3$ was used as the solvent.

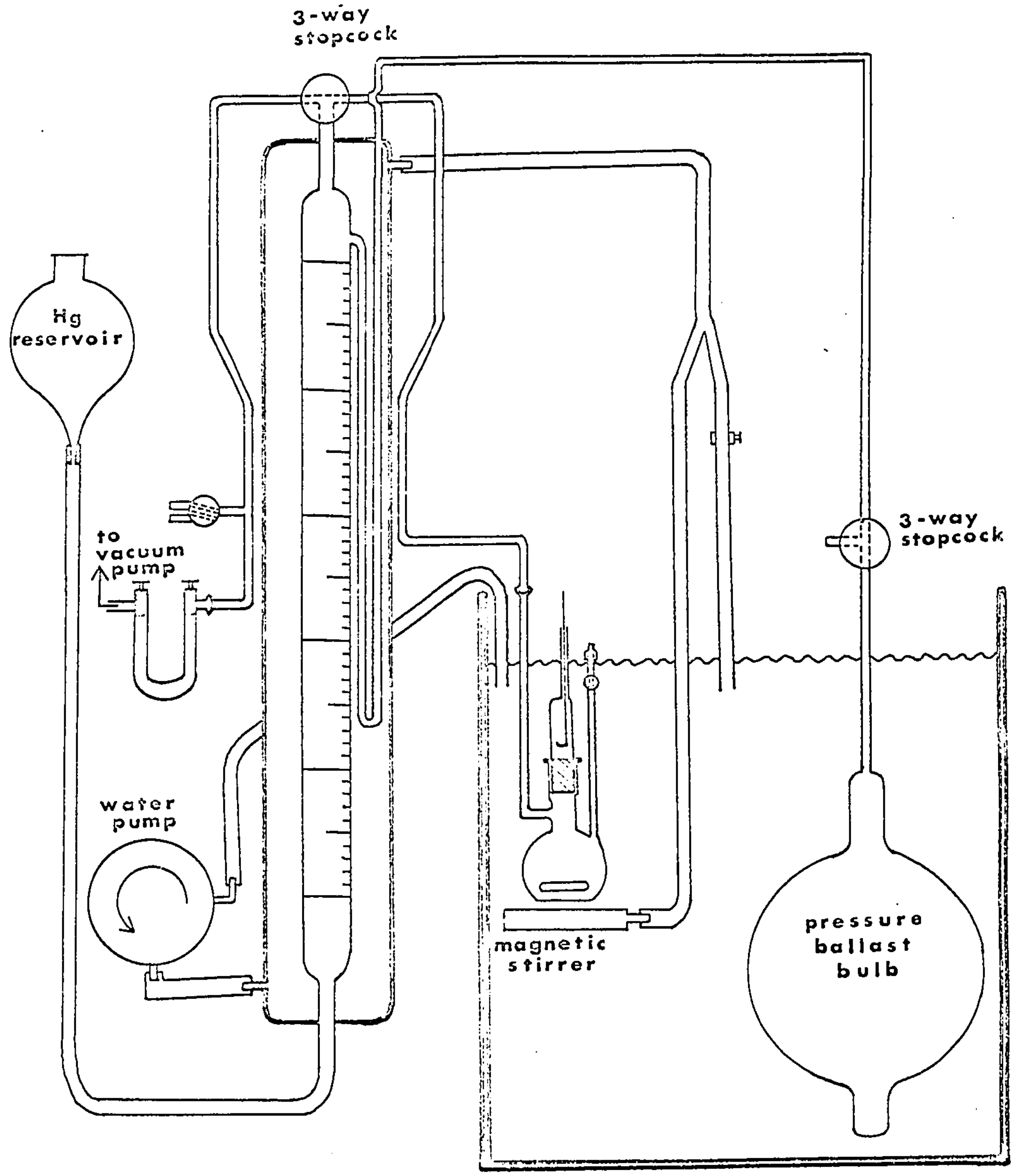
Equilibrium Measurements

Under appropriate conditions of ligand and CO concentrations, the reaction of $M(CO)_4$(X-o-phen) with L forms an equilibrium. Knowing the initial concentrations of L and $M(CO)_4$(X-o-phen), the equilibrium concentrations of $M(CO)_4$(X-o-phen) and CO, the concentrations of all the reactants and products at equilibrium can be determined and an equilibrium constant, K_{eq}, can be calculated. The equilibrium concentration of $M(CO)_4$(X-o-phen) was determined by measuring the absorbance of the highest frequency C-O stretching band of $M(CO)_4$(X-o-phen). Knowing its molar extinction coefficient one can calculate the concentration using Beer's law. The equilibrium concentration of CO was taken as the solubility of pure CO gas in o-dichlorobenzene at the temperature being studied.

The CO solubility and equilibrium measurements were carried out using the apparatus shown in Figure 6. This apparatus is a modification of one used elsewhere by Calderazzo and Cotton (17). The apparatus consists essentially of a thermostatted gas buret, a manometer and balast bulb for maintaining constant pressure, a reaction vessel, a water operated magnetic stirrer, and a vacuum system.

Using this apparatus the solubility of CO in the reaction solvent, o-dichlorobenzene, was determined at various

Figure 6. Constant pressure CO apparatus used in equilibrium constant determinations


3-way stopcock
Hg reservoir
to vacuum pump
water pump
magnetic stirrer
3-way stopcock
pressure ballast bulb

temperatures. This was done by first determining the volume of the system. The volume of the system was determined simply by pulling a high vacuum on the system (pressure measured with a Mc Leod gauge) and measuring the amount of gas necessary to fill the system to atmospheric pressure. Once the volume of the system was known, 25 ml. of solvent was pipetted into the reaction vessel (solvent volume being corrected for expansion from room temperature), and the manometer was filled with solvent (Hg was used in the apparatus volume determination). A strong vacuum was next pulled on the system for 10 minutes. A weighed cold trap located between the apparatus and the vacuum pump collected any solvent lost due to evaporation during the evacuation process. This trap was reweighed after the measurement and any necessary corrections were made in the solvent volume. After this period of time, pure CO at atmospheric pressure was let into the reaction vessel from the gas buret. The system was then allowed to equilibrate under vigorous stirring for 30 minutes, after which time the volume of gas let into the system from the gas buret was recorded. Knowing the free-volume of the system (total volume of the system minus volume of solvent present), the amount of CO introduced into the system, the barometric pressure, the equilibrium vapor pressure of the solvent at the temperature of the measurement, and the temperature, the solubility of CO gas in <u>o</u>-dichlorobenzene was calculated. A value of $\alpha = 0.0948$

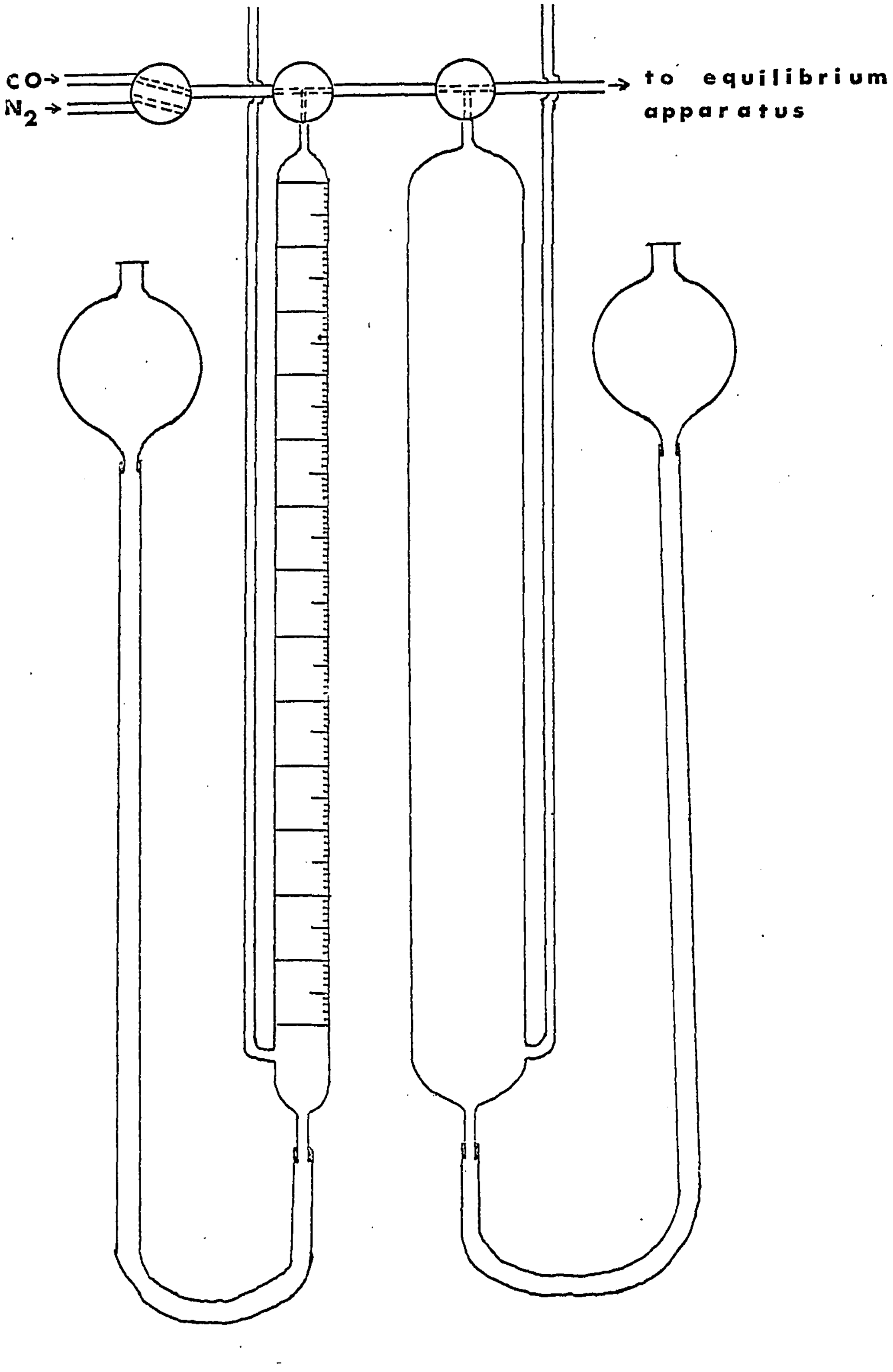
and 0.0980 at 45 and 60°, respectively were determined. Here α is the volume of CO, reduced to 0°C. and 1 atm., dissolved by 1 ml. of o-dichlorobenzene at the temperature of the experiment under a partial pressure of 1 atm. of CO. These values of α obtained here compare favorable with values of α determined elsewhere for the solubility of CO gas in other organic solvents (35).

A typical equilibrium constant determination was conducted in the following manner. Ten ml. of the ligand solution was pipetted into the reaction flask and a sample of the solid complex (usually between 20 and 60 mg.) was suspended above the ligand solution. The system was then allowed to thermally equilibrate for a short period of time before a strong vacuum was pulled on the system for about 3 minutes. After this time the vacuum was turned off and pure CO was introduced into the reaction flask from the CO tank or reservoir. This procedure of pulling a vacuum and introducing CO was then repeated two more times. After the third introduction of CO, the reaction flask was connected to the gas buret by means of the three-way stopcock. After adjusting the pressure inside of the apparatus to atmospheric pressure by means of the leveling bulb, the stopcock on the balast bulb was closed to hold the outside pressure constant. Once this had been done the sample was dropped into the ligand solution and allowed to react with vigorous stirring for between 6 and 20 hours. After equilibrium had been reached, a sample was withdrawn from the reaction flask through the serum cap and stopcock on the side of the flask by means of a 1 ml. syringe.

From the starting complexe's absorbance in the infrared, its equilibrium concentration and therefore the products concentration were easily determined. When the absorbance of $M(CO)_4$(X-o-phen) was measured in the infrared, the reference cell was filled with a solution containing the same ligand concentration as used in the equilibrium run. This technique cancelled out all of the extraneous absorbances due to the ligand.

For equilibrium measurements which were conducted at CO pressures other than atmospheric, the apparatus shown in Figure 7 was used to prepare the dilute CO mixtures. The desired amounts of CO and purified N_2 were measured out in the gas buret and stored in the reservoir. Equilibrium determinations were then carried out in the same manner as described above using this dilute CO mixture instead of pure CO. The concentration of CO in solution was calculated from the partial pressure of CO over the solvent. A very small correction was made in the total CO pressure of the fairly dilute CO mixtures because of the small amount of CO gas liberated during the reaction.

Figure 7. Apparatus used to prepare dilute CO mixtures of known CO and N_2 content


CO→
N_2→
→ to equilibrium apparatus

RESULTS

Kinetic Studies

Metal hexacarbonyls

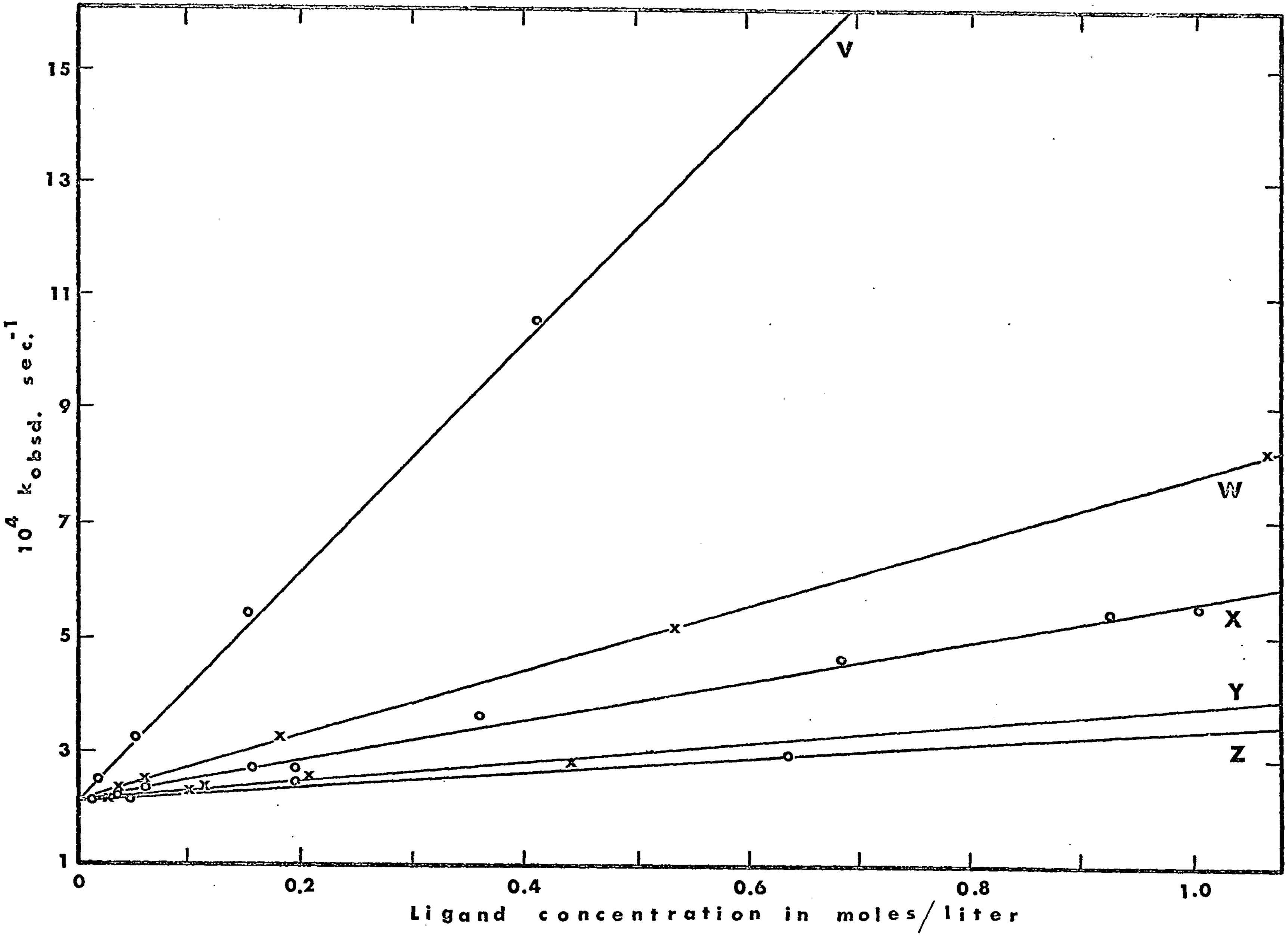
The metal hexacarbonyls of Group VI react with ligands, L, to form $M(CO)_5L$ as the initial reaction product (Equation 2). The rate of reaction follows a two-term rate law (Equation 3) over a large range of concentrations of L as is shown

$$\text{Rate} = k_1[M(CO)_6] + k_2[L][M(CO)_6] \qquad (3)$$

by the data in Tables 1, 2, and 3. In Figure 8 the pseudo-first order rate constants, $k_{obsd.}$, are plotted vs. the concentration of L for the reaction of $Mo(CO)_6$ with L at 112°C. The graph shows that $k_{obsd.}$ depends on [L] in the manner: $K_{obsd.} = k_1 + k_2[L]$. The value of $k_{obsd.}$ at $[L] = 0$ is k_1, and the slope of the line is k_2. As expected for a general rate law, k_1 is independent of the nature of L while k_2 definitely depends on L. The values of k_1 and k_2 determined for the reaction of $M(CO)_6$ with various ligands are listed in Table 4.

During the reaction of $P(\underline{n}\text{-}C_4H_9)_3$, L, with $Mo(CO)_6$ not only is $Mo(CO)_5L$ formed as a reaction product, but some $Mo(CO)_4L_2$ is formed as well. It results from the further reaction of $Mo(CO)_5L$ with excess L at a rate which is con-

Figure 8. Plot of $k_{obsd.}$ *vs.* ligand concentration for the reaction of $Mo(CO)_6$ with L at 112°C in decalin. V = $P(\underline{n}\text{-}C_4H_9)_3$, W = $P(OC_2H_5)_3$, X = $P(OCH_2)_3CC_2H_5$, Y = $P(C_6H_5)_3$, and Z = $P(OC_6H_5)_3$



$10^4 k_{obsd.}$ sec.$^{-1}$
15
13
11
9
7
5
3
1
0
0.2
0.4
0.6
0.8
1.0
Ligand concentration in moles/liter
V
W
X
Y
Z

siderably slower than the rate of reaction of $Mo(CO)_6$ with L. Therefore during a particular kinetic run most of the $Mo(CO)_6$ is converted to $Mo(CO)_5L$ before any substantial amount of $Mo(CO)_4L_2$ is formed. An attempt was made to quantitatively study the rate of reaction of $Mo(CO)_5L$ with L. But due to the higher temperatures necessary for this reaction, the only moderate stability of the complex, and the extreme sensitivity of the reaction rates to minute traces of air and other impurities, this was found to be impossible to do. However qualitatively it was determined that the rate of reaction of $Mo(CO)_5L$ with L followed a two-term rate law similar to Equation 3. The value of k_1 was approximately ¼ of the value obtained for the reaction of $Mo(CO)_6$ with L at the same temperature. The value of k_2 for the $Mo(CO)_5L$ reactions was also considerable smaller than those obtained for the $Mo(CO)_6$ reactions. In general the reactions of $Mo(CO)_5L$ with L do show second-order reaction kinetics and proceed at a slightly higher temperature than is required for the reaction of the metal hexacarbonyls with L.

For the reaction of $P(\underline{n}\text{-}C_4H_9)_3$ with $M(CO)_6$, the rates of reaction were determined at three different temperatures. From these temperature data entropies and enthalpies of activation were calculated for both parts of the observed rate law. These data along with their standard deviations are listed in Table 5. A non-linear least squares computer program[*] (43) was used to calculate the final values of the activation parameters and also the first and second order rate constants.

At about the same time this study was being carried out, Werner and Prinz in Germany made an independent study (66) of the reaction of the Group VI metal hexacarbonyls with various ligands using a mixture of decane and cyclohexane as the reaction solvent. They conducted their study using very low ligand concentrations (between 1 and 10 times the concentration of the metal hexacarbonyl) and because of this observed only the ligand independent term of the two-term rate law. Their data for this portion of the rate law, as typified by the values listed in Table 5, are in very good agreement with the data obtained in this study.

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[*] Thanks is given to Mr. J. P. Birk for modification of this program for use on the present computer facilities.

Table 1. Rate constants for the reaction of $Cr(CO)_6$ with L in decalin

Ligand	Temperature ^oC	[L] moles/liter	$10^{-4}k_{osbd.}$ $sec.^{-1}$
$P(\underline{n}\text{-}C_4H_9)_3$	130.7	0.0168	1.38
		0.0719	1.41
		0.138	1.60
		0.376	1.66
		0.696	1.98
	135.5	0.0176	2.39
		0.0344	2.46
		0.133	2.58
		0.404	2.86
		0.909	3.55
	143.9	0.0157	6.75
		0.0368	6.81
		0.125	6.90
		0.396	7.77
		0.917	8.93
$P(C_6H_5)_3$	130.7	0.0140	1.38
		0.0476	1.40
		0.0927	1.51
		0.200	1.45
		0.444	1.56
$P(OC_6H_5)_3$	130.7	0.0169	1.32
		0.0850	1.35
		0.247	1.53
		0.481	1.59
		0.843	1.76

Table 2. Rates of reaction of $Mo(CO)_6$ with various ligands in decalin

Ligand	Temperature ^oC	[L] moles/liter	$10^4k_{osbd.}$ $sec.^{-1}$
$P(\underline{n}-C_4H_9)_3$	103.4	0.0142	1.11
		0.0587	1.59
		0.128	2.48
		0.404	5.44
		0.805	9.34
	106.6	0.0159	1.59
		0.0533	2.14
		0.141	3.56
		0.454	8.00
		0.800	11.5
	112.0	0.0176	2.43
		0.0489	3.24
		0.149	5.47
		0.408	10.5
		0.828	18.9
	116.4	0.0164	4.57
		0.583	6.13
		0.146	8.79
		0.469	18.2
		0.856	30.7
$P(OC_2H_5)_3$	112.0	0.0325	2.51
		0.0625	2.66
		0.183	3.52
		0.529	5.32
		1.058	8.46
$P(OCH_2)_3CC_2H_5$	112.0	0.0345	2.26
		0.195	2.70
		0.357	3.61
		0.682	4.61
		0.922	5.42
		1.010	5.49

Table 2 (Continued)

Ligand	Temperature °C	[L] moles/liter	$10^4k_{osbd.}$ sec.$^{-1}$
$P(C_6H_5)_3$	112.0	0.0214	2.06
		0.0251	2.18
		0.0333	2.23
		0.100	2.30
		0.114	2.37
		0.206	2.58
		0.440	2.82
$P(OC_6H_5)_3$	112.0	0.0107	2.14
		0.0450	2.19
		0.188	2.47
		0.631	3.04
		0.814	3.27
$As(C_6H_5)_3$	112.00	0.0107	2.14
		0.0378	2.17
		0.144	2.51
		0.688	2.73
		0.492	2.75

Table 3. Rates of reaction of $W(CO)_6$ with various ligands in decalin

Ligand	Temperature °C	[L] moles/liter	$10^4k_{obsd.}$ sec.$^{-1}$
$P(\underline{n}\text{-}C_4H_9)_3$	145.9	0.00842	0.146
		0.0437	0.185
		0.115	0.327
		0.379	0.658
		0.896	1.37
	155.5	0.0157	0.398
		0.568	0.698
		0.182	1.20
		0.453	2.34
		0.864	3.77

Table 3 (Continued)

Ligand	Temperature °C	[L] moles/liter	$10^4 k_{obsd.}$ sec.$^{-1}$
	165.7	0.0175	1.33
		0.0752	1.76
		0.151	2.20
		0.478	4.63
		0.836	7.02
$P(OCH_2)_3CC_2H_5$	165.7	0.0154	1.10
		0.0661	1.22
		0.244	1.42
		0.459	1.80
		0.876	2.49
$P(C_6H_5)_3$	165.7	0.00966	1.11
		0.0417	1.15
		0.130	1.19
		0.229	1.32
		0.382	1.54
$P(OC_2H_5)_3$	165.7	0.0242	1.15
		0.123	1.49
		0.311	1.68
		0.598	2.14
$P(\underline{n}\text{-}C_4H_9)_3$	175.4	0.0185	3.83
		0.0550	3.98
		0.282	7.83
		0.554	13.0

Table 4. Rate constants for the reaction of $M(CO)_6$ with various ligands in decalin

		$Cr(CO)_6$[a]		$Mo(CO)_6$[b]		$W(CO)_6$[c]	
L	Δ_{HNP}[d]	$10^4 k_1$ (sec.$^{-1}$)	$10^4 k_2$ (l/mole sec.)	$10^4 k_1$ (sec.$^{-1}$)	$10^4 k_2$ (l/mole sec.)	$10^4 k_1$ (sec.$^{-1}$)	$10^4 k_2$ (l/mole sec.)
$P(n\text{-}C_4H_9)_3$	131	1.38	0.854	2.13	20.5	1.15	7.10
$P(OC_2H_5)_3$	520	1.38	0.450	2.13	6.69	1.15	1.70
$P(OCH_2)_3CC_2H_5$				2.13	3.56	1.15	1.48
$P(C_6H_5)_3$	573	1.38	0.431	2.13	1.77	1.15	0.888
$P(OC_6H_5)_3$	875			2.13	1.48		
$As(C_6H_5)_3$				2.13	1.03		

[a] At 130.7°.

[b] At 112.0°.

[c] At 165.0°.

[d] See reference 59.

$M(CO)_4(N-N)$

Complexes of the type $M(CO)_4(N-N)$, where M = Cr, Mo, or W and N-N = 2,2'-dipyridyl, 4,4'-dimethyl-2,2'-dipyridyl, X-*o*-phenanthroline, or 1,2-diamino-2-methylpropane, react with ligands, L, to form *cis*-$M(CO)_3(N-N)L$ as the main reaction product. In the case where the central metal atom is Cr and N-N is any of the bidentate ligands except 1,2-diamino-2-methylpropane this is the only metal carbonyl reaction product. When the complex is $Cr(CO)_4$(diamine), where diamine = 1,2-diamino-2-methylpropane, not only is *cis*-$Cr(CO)_3$(diamine)L formed but also some *cis*-$Cr(CO)_3L_3$. This product results from the further reaction of $Cr(CO)_3$(diamine)L with excess L. Also for M = Mo and W and N-N = X-*o*-phen the only product formed is *cis*-$M(CO)_3(N-N)L$. However for M = Mo and W and N-N being any of the bidentate ligands studied except X-*o*-phen, some *cis*-$M(CO)_4L_2$ and *cis*-$M(CO)_3L_3$ are also formed as reaction products.

The assignment of the configuration of $M(CO)_3(N-N)L$ as the *cis* isomer was made on the basis of the infrared spectra of the complexes. The *cis* configuration is the only assignment possible which is consistent with the three strong CO absorptions in the infrared (Table 17). This assignment is also the same as the one made earlier by Stiddard (55) for the analogous complexes of $Mo(CO)_3$(dipy)L where L was triphenyl phosphine and pyridine.

Table 5. Activation parameters for the reaction of Group VI metal carbonyl complexes with various ligands, L

Complex	Ligand L	$\Delta H_1^\ddagger$ kcal./mole	$\Delta S_1^\ddagger$ e.u.	$\Delta H_2^\ddagger$ kcal./mole	$\Delta S_2^\ddagger$ e.u.
		In decalin			
$Cr(CO)_6$	$P(\underline{n}\text{-}C_4H_9)_3$	40.2 ± 0.6 $(38.4)^a(38.1)^b$	22.6 ± 1.5 $(17.7)^b$	25.5 ± 2.9	-14.6 ± 7.0
$Mo(CO)_6$	$P(\underline{n}\text{-}C_4H_9)_3$	31.7 ± 1.4 $(30.2)^a(30.2)^b$	6.7 ± 3.7 $(2.7)^b$	21.7 ± 1.3	-14.9 ± 3.4
$W(CO)_6$	$P(\underline{n}\text{-}C_4H_9)_3$	39.9 ± 1.6 $(39.8)^a(39.0)^b$	13.8 ± 3.7 $(11.6)^b$	29.2 ± 1.6	-6.9 ± 3.8
		In 1,2-dichloroethane			
$Cr(CO)_4$(3,4,7,8-tetramethyl-$\underline{o}$-phen)	$P(OCH_2)_3CCH_3$	25.2 ± 0.1	5.2 ± 0.3		
$Cr(CO)_4(\underline{o}\text{-phen})$	$P(OCH_2)_3CCH_3$	26.4 ± 0.8	7.0 ± 2.6		
$Mo(CO)_4(\underline{o}\text{-phen})$	$P(OCH_2)_3CCH_3$	25.1 ± 1.2	2.4 ± 2.4	19.1 ± 1.2	-17.0 ± 2.0
$Cr(CO)_4(dipy)$	$P(OC_2H_5)_3$	24.3 ± 0.3	1.9 ± 0.9		
	$P(OCH_2)_3CCH_3$	23.4 ± 0.1	-1.1 ± 0.3		
	$PO_3C_6H_9$	25.4 ± 0.2	5.1 ± 0.6		
$Mo(CO)_4(dipy)$	$PO_3C_6H_9$	21.5 ± 0.9	-9.1 ± 2.8	18.6 ± 0.7	-15.4 ± 2.3
	$P(OC_2H_5)_3$	24.6 ± 0.7	0.5 ± 2.1	21.3 ± 0.8	-9.4 ± 2.6
	$P(OCH_2)_3CCH_3$	23.7 ± 0.9	-2.3 ± 2.9	20.8 ± 0.7	-10.0 ± 2.1
		In chlorobenzene			
$Cr(CO)_4(dipy)$	$P(OC_2H_5)_3$	22.6 ± 0.1	-5.4 ± 0.2		
	$P(OCH_2)_3CCH_3$	28.6 ± 0.1	13.6 ± 0.3		
	$PO_3C_6H_9$	24.4 ± 1.0	0.5 ± 3.0		
$Mo(CO)_4(dipy)$	$PO_3C_6H_9$	23.9 ± 1.1	-2.5 ± 3.4	17.0 ± 0.7	-20.5 ± 2.2
	$P(OC_2H_5)_3$	27.3 ± 1.3	7.5 ± 4.0	13.6 ± 1.2	-33.4 ± 3.6
	$P(OCH_2)_3CCH_3$	28.9 ± 0.7	12.5 ± 2.2	12.3 ± 0.7	-37.2 ± 2.3
$W(CO)_4(dipy)$	$PO_3C_6H_9$	24.6 ± 6.1	-12.5 ±15.8	24.2 ± 2.2	-10.9 ± 5.7
	$P(OC_2H_5)_3$	26.1 ± 1.3	-7.5 ± 3.4	20.0 ± 1.2	-20.8 ± 3.2
$W(CO)_4(\underline{o}\text{-phen})$	$P(OCH_2)_3CCH_3$	33.4 ± 1.0	-10.6 ± 3.0	23.6 ± 0.8	-37.6 ± 2.8

[a] Data obtained from rates of ^{14}CO exchange in the gas phase. See references 18 and 47.

[b] Results of Werner and Prinz. See reference 66.

The complex $M(CO)_3L_3$ was assigned the cis configuration because of its two strong equally intense absorptions in the C-O stretching region of the infrared. The infrared spectrum of this complex is consistent with a compound having C_{3v} point group symmetry (20). This is also the same assignment made by Poilblanc and Bigorgne (52) for some other trisubstituted complexes having similar infrared spectra. The complex $M(CO)_4L_2$ formed by the replacement of the bidentate ligand, N-N, with two L groups was assigned the cis configuration from the infrared and N.M.R. spectra of the complexes, both being consistent with this assignment (64). Also this is the isomer that would be expected from the reaction.

As shown by the data in Tables 6, 7, and 8, the rate of reaction of $Cr(CO)_4(N\text{-}N)$ with L follows a simple first-order rate law (Equation 4) and is independent of the concentration and nature of the entering ligand. However when the complex was $Cr(CO)_4(dipy)$, the rate appeared to depend slightly on the nature of the entering ligand. The slight dependence of the reaction rates and also the activation parameters (Table 5) on the nature of the incoming ligand seemed to be outside of experimental error and could be

$$\text{Rate} = k_1[Cr(CO)_4(N\text{-}N)] \qquad (4)$$

Table 6. Rates of reaction of $Cr(CO)_4(dipy)$ with phosphites in 1,2-dichloroethane

Phosphite	[L], moles/l.	Temp., °C.	$10^5 k_{obsd.}$ sec.$^{-1}$
$P(OC_2H_5)_3$	0.111	37.8	13.4
	1.00	37.8	13.5
	1.30	37.8	13.5
	0.0089	47.9	43.1
	0.0297	47.9	44.8
	0.0322	47.9	45.4
	0.0594	47.9	49.3
	0.111	47.9	51.6
	0.550	47.9	51.2
	0.779	47.9	51.1
	0.403	58.1	158
	0.574	58.1	163
	0.725	58.1	159
$P(OCH_2)_3CCH_3$	0.156	37.8	13.4
	0.656	37.8	13.6
	1.41	37.8	14.0
	0.0056	47.9	43.7
	0.0224	47.9	47.8
	0.0625	47.9	45.8
	0.0625	47.9	49.1
	0.365	47.9	46.8
	0.658	47.9	46.5
	1.09	47.9	46.7
	0.156	58.1	149
	1.09	58.1	147
	1.41	58.1	148
$PO_3C_6H_9$	0.0873	37.8	10.8
	0.271	37.8	11.2
	0.677	37.8	11.4

Table 6 (Continued)

Phosphite	[L], moles/l.	Temp., °C.	$10^5k_{obsd.}$ sec.$^{-1}$
	0.0045	47.9	42.9
	0.0239	47.9	45.8
	0.0559	47.9	46.6
	0.0873	47.9	43.7
	0.338	47.9	43.8
	0.773	47.9	43.9
	0.0873	58.1	146
	0.338	58.1	148
	0.676	58.1	149

Table 7. Rates of reaction of $Cr(CO)_4(dipy)$ with phosphites in chlorobenzene

Phosphite	[L], moles/l.	Temp.c °C.	$10^5k_{obsd.}$ sec.$^{-1}$
$P(OC_2H_5)_3$	0.114	37.8	5.57
	0.798	37.8	5.57
	0.114	47.9	18.3
	0.798	47.9	17.9
	0.114	58.1	55.8
	0.798	58.1	55.8
$P(OCH_2)_3CCH_3$	0.106	37.8	4.88
	1.69	37.8	4.92
	0.365	47.9	21.4
	1.09	47.9	21.3
	0.156	58.1	89.4
	1.27	58.1	89.7

Table 7 (Continued)

Phosphite	[L], moles/l.	Temp., °C.	$10^5k_{obsd.}$ sec.$^{-1}$
$PO_3C_6H_9$	0.150	37.8	6.20
	0.451	37.8	6.17
	0.0178	47.9	18.4
	0.137	47.9	18.4
	0.150	58.1	75.2
	0.451	58.1	75.1

Table 8. Rates of reaction of $Cr(CO)_4$(X-o-phen) and $Cr(CO)_4$(1,2-diamino-2-methylpropane) with $P(OCH_2)_3CCH_3$ in 1,2-dichloroethane at 47.9°

X-o-phen number	X	$[P(OCH_2)_3CCH_3]$ moles/liter	$10^4k_{obsd.}$, sec.$^{-1}$
1	5,6-dichloro	0.0662	1.34
	3.47[a]	0.543	1.36
		1.16	1.33
2	5-nitro	0.0284	1.08
	3.57	0.284	1.10
		0.800	1.13
3	4,7-diphenyl	0.0284	2.62
	4.84	0.284	2.66
		0.800	2.67

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[a] Numbers below names are pK_a values of the respective o-phenanthroline. See reference 53.

Table 8 (Continued)

X-*o*-phen number	X	$[P(OCH_2)_3CCH_3]$ moles/liter	$10^4 k_{obsd.}$, $sec.^{-1}$
4	unsubstituted	0.00783	0.593[b]
	4.86	0.0365	0.590[b]
		0.0662	0.570[b]
		0.543	0.590[b]
		0.903	0.582[b]
		0.0662	1.63[c]
		0.543	1.63[c]
		0.903	1.62[c]
		0.0662	2.73
		0.543	2.68
		1.16	2.72
		0.0662	4.56[d]
		0.543	4.63[d]
		0.903	4.60[d]
		0.0662	9.27[e]
		0.302	9.27[e]
		0.543	9.29[e]
5	3-methyl	0.0662	2.80
	5.00	0.543	2.79
		1.16	2.76
6	3,5,7-trimethyl	0.0662	4.84
	5.90	0.543	4.82
		1.16	4.83
7	3,4,7,8-tetramethyl	0.0662	1.66[b]
	6.31	0.543	1.66[b]
		0.903	1.65[b]
		0.0662	3.26[c]

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[b] At 37.8°.

[c] At 42.9°.

[d] At 53.0°.

[e] At 58.0°.

Table 8 (Continued)

X-o-phen number	X	$[P(OCH_2)_3CCH_3]$ moles/liter	$10^4 k_{obsd.}$, sec.$^{-1}$
		0.543	3.29^c
		0.903	3.30^c
		0.0662	6.14
		0.543	6.11
		0.903	6.10
		0.0662	11.6^d
		0.302	11.7^d
		0.543	11.6^d
		0.0662	21.5^e
		0.302	21.5^e
		0.543	21.6^e
8	3,4,6,7-tetramethyl	0.0662	7.17
	6.45	0.543	7.18
		1.16	7.17
$Cr(CO)_4$(1,2-diamino-2-methylpropane)		0.0126	48.0
		0.0247	50.0
		0.0884	45.0
		0.139	44.0
		1.09	43.0
		1.41	47.0

explained by an association of the reacting complex with the ligand. In an attempt to obtain some independent evidence for this interaction, the solubility of $Cr(CO)_4$(dipy) in pure 1,2-dichloroethane and in 1,2-dichloroethane containing varying amounts of ligand was determined spectrophotometrically. The molar extinction coefficient of $Cr(CO)_4$(dipy) was determined and found to be 1080 l./mole cm. Its value was found to be unaffected by the ligand concentrations used in the solubility study. $Cr(CO)_4$(dipy) has a solubility of 0.0110 mole/l. at 25° in pure 1,2-dichloroethane. This solubility increases for ligand concentrations of 0.008 to 0.200 M by about 1% for $P(OC_2H_5)_3$, 4% for $P(OCH_2)_3CCH_3$, and 10 to 14% for $PO_3C_6H_9$. The relative independence of the solubility of $Cr(CO)_4$(dipy) in a ligand solution of concentration greater than 0.008 M on the ligand concentration indicates that there is virtually no association between the complex and ligand at 25°.

It might be expected that any association between the ligand and complex would alter the position of the C-O absorptions in $Cr(CO)_4$(dipy). In an experiment to detect the slightest shift in absorption, a solution of $Cr(CO)_4$(dipy) in 1,2-dichloroethane was placed in the reference cell of the double beam spectrophotometer, and a solution of the same complex concentration but containing added $P(OCH_2)_3CCH_3$ was placed in the sample beam. This differential spectrum showed absolutely no difference between the two solutions.

If some associated species were a reactive form of the complex, an equilibrium between the free complex and this species would result in a ligand dependence of the reaction rate at low ligand concentrations. Because the reaction being measured came to equilibrium at these concentrations, initial rates were determined. As the ligand concentrations were decreased, these rates appeared to decrease slightly at

47.9°. While a decrease would suggest complex-ligand association, the observed decrease is so small and almost within experimental error even for $P(OC_2H_5)_3$, which exhibited the largest apparent change in rate, that it is not possible to say that the kinetic data definitely indicate association.

Since the solubility and infrared studies strongly suggest that there is no association between the complex and ligand, and the kinetic studies are inconclusive, it appears that the slight variations in the first order rates and activation parameters are due to some other interaction than complex-ligand association before reaction. It is not clear at what point the ligand exerts its effect.

When the central metal atom, M, is Mo or W, the rate of reaction of $M(CO)_4(N\text{-}N)$ with L is no longer first order (Tables 9, 10, 11, 12, and 13), but a two-term rate law similar to the one followed for the metal hexacarbonyl reactions is observed (Equation 5). As in the metal hexacarbonyl reactions k_1 is essentially independent of the

$$\text{Rate} = k_1[M(CO)_4(N\text{-}N)] + k_2[L][M(CO)_4(N\text{-}N)] \qquad (5)$$

nature of L and k_2 is definitely dependent on L. The values of k_1 and k_2 determined are listed in Tables 14 and 15.

The value of k_1 is strictly independent of the nature of the ligand under consideration except for the case where

Table 9. Rates of reaction of $Mo(CO)_4(dipy)$ with phosphites in 1,2-dichloroethane

Phosphite L	[L], moles/l.	Temp., °C	$10^5k_{obsd.}$, sec.$^{-1}$
$P(OCH_2)_3CCH_3$	0.156	37.8	6.56
	0.656	37.8	11.6
	1.41	37.8	19.8
	1.82	37.8	24.6
	0.00592	47.9	15.7
	0.0182	47.9	16.3
	0.156	47.9	19.6
	0.365	47.9	26.1
	0.518	47.9	30.1
	0.518	47.9	31.3
	0.656	47.9	34.4
	1.09	47.9	47.7
	0.156	58.1	66.3
	0.365	58.1	82.9
	0.656	58.1	109
	1.09	58.1	155
	1.41	58.1	178
	1.64	58.1	198
$PO_3C_6H_9$	0.0873	37.8	7.86
	0.270	37.8	11.8
	0.451	37.8	17.4
	0.676	37.8	22.2
	0.00394	47.9	16.8
	0.0170	47.9	17.1
	0.148	47.9	26.4
	0.338	47.9	42.1
	0.452	47.9	49.3
	0.580	47.9	58.2
	0.0873	58.1	65.6
	0.338	58.1	103
	0.541	58.1	138
	0.676	58.1	167

Table 9 (Continued)

Phosphite L	[L], moles/l.	Temp., °C	$10^5k_{obsd.}$, $sec.^{-1}$
$P(OC_2H_5)_3$	0.111	37.8	5.12
	0.569	37.8	8.07
	0.779	37.8	10.0
	1.00	37.8	10.7
	1.30	37.8	12.6
	0.00562	47.9	15.9
	0.0228	47.9	16.3
	0.136	47.9	17.5
	0.319	47.9	21.4
	0.574	47.9	26.0
	0.956	47.9	32.6
	1.243	47.9	36.5
	0.136	58.1	61.8
	0.136	58.1	62.2
	0.318	58.1	69.4
	0.574	58.1	84.3
	1.21	58.1	119
	1.55	58.1	144
	1.81	58.1	164

Table 10. Rates of reaction of $M(CO)_4$(dipy) with phosphites in chlorobenzene

Phosphite L	[L], moles/l.	Temp., °C	$10^5k_{obsd.}$, $sec.^{-1}$
	$Mo(CO)_4$(dipy)		
$P(OCH_2)_3CCH_3$	0.0576	37.8	2.38
	0.105	37.8	2.93
	0.120	37.8	3.26
	0.198	37.8	4.10
	0.238	37.8	4.37
	0.276	37.8	4.82
	0.394	37.8	5.87
	1.36	37.8	17.0

Table 10 (Continued)

Phosphite L	[L], moles/l.	Temp., °C	$10^5 k_{obsd.}$, sec.$^{-1}$
	0.156	47.9	9.84
	0.365	47.9	15.4
	0.656	47.9	21.0
	1.094	47.9	29.6
	1.41	47.9	35.6
	1.64	47.9	40.0
	0.0662	58.1	34.8
	0.161	58.1	38.2
	0.307	58.1	45.4
	0.440	58.1	51.9
	0.563	58.1	56.0
	0.780	58.1	69.7
	0.965	58.1	71.8
	1.266	58.1	84.6
	1.688	58.1	100.0
$P(OC_2H_5)_2$	0.114	37.8	2.86
	0.174	37.8	3.52
	0.266	37.8	3.90
	0.479	37.8	6.18
	0.798	37.8	8.72
	1.02	37.8	10.4
	0.114	47.9	9.84
	0.266	47.9	12.1
	0.479	47.9	17.4
	0.798	47.9	24.7
	1.025	47.9	28.4
	1.20	47.9	30.7
	0.317	58.1	42.2
	0.492	58.1	49.3
	0.982	58.1	61.4
	1.41	58.1	74.8
$PO_3C_6H_9$	0.150	37.8	6.27
	0.214	37.8	8.42
	0.271	37.8	9.64
	0.451	37.8	14.5
	0.580	37.8	16.6

Table 10 (Continued)

Phosphite L	[L], moles/l.	Temp., °C	$10^5 k_{obsd.}$, $sec.^{-1}$
	0.150	47.9	19.1
	0.214	47.9	23.8
	0.271	47.9	27.3
	0.451	47.9	39.2
	0.580	47.9	44.2
	0.0727	58.1	43.4
	0.0908	58.1	44.0
	0.104	58.1	48.2
	0.311	58.1	79.2
	0.395	58.1	84.8
$P(OC_2H_5)_3$	0.362	100.0	12.3
	0.671	100.0	19.2
	1.09	100.0	27.7
	1.40	100.0	35.2
	1.63	100.0	39.6
	0.266	110.0	27.2
	0.378	110.0	35.2
	0.479	110.0	43.5
	1.02	110.0	76.7
	1.20	110.0	92.0
	0.362	120.0	71.4
	0.514	120.0	86.5
	0.671	120.0	109
	1.09	120.0	151
	1.81	120.0	236
$PO_3C_6H_9$	0.128	100.0	15.3
	0.271	100.0	22.4
	0.451	100.0	28.9
	0.580	100.0	34.7
	0.150	110.0	36.4
	0.271	110.0	49.4
	0.338	110.0	58.2
	0.451	110.0	65.4
	0.541	110.0	74.2

Table 10 (Continued)

Phosphite L	[L], moles/l.	Temp., °C	$10^5k_{obsd.}$, sec.$^{-1}$
	0.150	120.0	89.0
	0.214	120.0	101
	0.271	120.0	112
	0.451	120.0	142
	0.580	120.0	160

Table 11. Rates of reaction of $Mo(CO)_4$(X-o-phen) with $P(OCH_2)_3CCH_3$ in 1,2-dichloroethane at 47.9°C

X-o-phen number	X	$[P(OCH_2)_3CCH_3]$ moles/liter	$10^4k_{obsd.}$ sec.$^{-1}$
1	5,6-dichloro	0.0284	0.668
		0.0800	0.792
		0.200	1.08
		0.400	1.63
		0.800	2.52
2	5-nitro	0.0284	0.628
		0.0800	0.832
		0.200	1.21
		0.400	1.79
		0.800	2.87
3	4,7-diphenyl	0.0284	1.06
		0.0800	1.14
		0.200	1.21
		0.400	1.34
		0.800	1.51
4	unsubstituted	0.0776	1.22
		0.156	1.37
		0.365	1.58
		0.656	1.83
		1.09	2.50
		1.41	2.74

Table 11 (Continued)

X-$\underline{o}$-phen number	X	$[P(OCH_2)_3CCH_3]$ moles/liter	$10^4k_{obsd.}$ sec.$^{-1}$
5	3-methyl	0.0776	1.33
		0.3650	1.59
		0.518	1.70
		1.411	2.64
6	3,5,7-trimethyl	0.156	1.75
		0.365	1.95
		0.656	2.18
		1.41	2.65
7	3,4,7,8-tetramethyl	0.0776	2.04
		0.365	2.28
		0.656	2.48
		1.09	2.74
8	3,4,6,7-tetramethyl	0.156	2.26
		0.365	2.37
		0.656	2.49
		1.41	2.86

Table 12. Rates of reaction of $Mo(CO)_4$(X-$\underline{o}$-phen) and $Mo(CO)_4$(1,2-diamino-2-methylpropane) with L in 1,2-dichloroethane at 47.9°

L	[L] moles/liter	$10^4k_{obsd.}$ sec^{-1}
	$Mo(CO)_4$($\underline{o}$-phen)	
$PO_3C_6H_9$	0.0266	1.17
	0.193	1.70
	0.541	2.90
	0.846	3.64
$P(OC_2H_5)_3$	0.0340	1.04
	0.0912	1.13
	0.228	1.24
	0.456	1.36
	0.911	1.63

Table 12 (Continued)

L	[L] moles/liter	$10^4k_{obsd.}$ sec.$^{-1}$
$P(C_6H_5)_3$	0.0229	1.14
	0.106	1.19
	0.334	1.20
	0.584	1.20
$P(OC_6H_5)_3$	0.0342	1.15
	0.159	1.17
	0.498	1.16
	0.873	1.19
	$Mo(CO)_4$(4,7-diphenyl-_o_-phen)	
$PO_3C_6H_9$	0.0266	1.16
	0.193	1.50
	0.541	2.12
	0.846	2.68
$P(OC_2H_5)_3$	0.0340	1.04
	0.0912	1.14
	0.228	1.31
	0.456	1.59
	0.911	2.01
$P(C_6H_5)_3$	0.0285	1.07
	0.130	1.09
	0.389	1.09
	0.648	1.09
	$Mo(CO)_4$(1,2-diamine-2-methylpropane)	
$P(OCH_2)_3CCH_3$	0.0584	1.11
	0.156	2.00
	0.365	3.72
	0.520	5.31
	0.656	5.93

Table 13. Rates of reaction of $W(CO)_4(X\text{-}o\text{-}phen)$ with L in chlorobenzene

L	Temp. °C	[L] moles/liter	$10^4k_{obsd.}$ sec.$^{-1}$
		$W(CO)_4(o\text{-}phen)$	
$P(n\text{-}C_4H_9)_3$	114.0	0.2099	1.76
		0.0898	2.00
		0.224	2.67
		0.449	3.81
		0.898	6.01
$P(OC_2H_5)_3$	114.0	0.0258	1.66
		0.0775	1.96
		0.194	2.28
		0.487	3.45
		0.775	4.44
$P(OCH_2)_3CCH_3$	106.2	0.0259	0.716
		0.103	0.943
		0.194	1.10
		0.388	1.42
		0.776	2.11
	114.0	0.0259	1.71
		0.103	2.12
		0.194	2.31
		0.388	3.06
		0.776	4.27
	122.8	0.115	5.41
		0.218	6.26
		0.436	7.87
		0.861	10.7
$P(C_6H_5)_3$	114.0	0.0207	1.62
		0.0610	1.57
		0.155	1.70
		0.310	1.67
		0.620	1.68
		$W(CO)_4(5\text{-nitro-}o\text{-phen})$	
$P(OCH_2)_3CCH_3$	114.0	0.0259	1.28
		0.103	1.52
		0.194	2.17
		0.388	3.52
		0.776	5.82

Table 13 (Continued)

L	Temp. °C	[L] moles/liter	$10^4 k_{obsd.}$ sec.$^{-1}$
	$W(CO)_4$(3,4,7,8-tetramethyl-o-phen)		
$P(OCH_2)_3CCH_3$	114.0	0.0259	3.76
		0.103	4.00
		0.194	4.35
		0.388	4.73
		0.776	5.69

the bidentate ligand was 2,2'-dipyridyl. For the reactions of this complex with L, the values of k_1 and the activation parameters for the k_1 part of the rate law seemed to vary with the nature of L by amounts which appeared to be outside of experimental error. The variations in the value of k_1 for the $Mo(CO)_4$(dipy) and $W(CO)_4$(dipy) reactions were analogous to the variations in k_1 observed for the $Cr(CO)_4$(dipy) reactions.

For the $Cr(CO)_4$(dipy) reactions, complex solubilities and initial rate constants determined at low ligand concentrations seemed to indicate that association between the complex and the ligand was probably not responsible for the variation in the first-order rate constants. In an effort to ascertain if this was also the case for the $Mo(CO)_4$(dipy) and $W(CO)_4$(dipy) reactions, the following were determined: the solubility of $Mo(CO)_4$(dipy) in pure 1,2-dichloroethane and in 1,2-dichloroethane containing varying amounts of L,

Table 14. Rate constants for the reaction of $M(CO)_4(X\text{-}\underline{o}\text{-phen})$ with $P(OCH_2)_3CCH_3$

X	No.	pK_a[c]	$Cr(CO)_4(X\text{-}\underline{o}\text{-phen})$[a] 10^4k_1 ($sec.^{-1}$)	10^4k_2 (l/mole sec.)	$Mo(CO)_4(X\text{-}\underline{o}\text{-phen})$[a] 10^4k_1 ($sec.^{-1}$)	10^4k_2 (l/mole sec.)	$W(CO)_4(X\text{-}\underline{o}\text{-phen})$[b] 10^4k_1 ($sec.^{-1}$)	10^4k_2 (l/mole sec.)
5,6-dichloro	1	3.47	1.34	0.0	.610	2.41		
5-nitro	2	3.57	1.10	0.0	.600	2.87	1.01	6.22
4,7-diphenyl	3	4.84	2.65	0.0	1.09	.547		
unsubstituted	4	4.86	2.71	0.0	1.14	1.16	1.63	3.48
3-methyl	5	5.00	2.79	0.0	1.23	.993		
3,5,7-trimethyl	6	5.90	4.83	0.0	1.68	.703		
3,4,7,8-tetramethyl	7	6.31	6.12	0.0	2.01	.696	3.76	2.51
3,4,6,7-tetramethyl	8	6.45	7.17	0.0	2.19	.475		
1,2-diamino-2-methylpropane		1) 10.00 2) 6.79	46.0	0.0	6.93	82.3		

[a] Rate constants determined in 1,2-dichloroethane at 47.9°C.

[b] Rate constants determined in chlorobenzene at 114.0°C.

[c] Values as reported by A. A. Schilt and G. F. Smith, (53).

Table 15. Rate constants for the reaction of $M(CO)_4$(o-phen) and $Mo(CO)_4$(4,7-diphenyl-o-phen) with L

	$Mo(CO)_4$(o-phen)[a]		$Mo(CO)_4$(4,7-diphenyl-o-phen)[a]		$W(CO)_4$(o-phen)[b]	
L	10^4k_1 ($sec.^{-1}$)	10^4k_2 (l./mole sec.)	10^4k_1 ($sec.^{-1}$)	10^4k_2 (l./mole sec.)	10^4k_1 ($sec.^{-1}$)	10^4k_2 (l./mole sec.)
$P(n\text{-}C_4H_9)_3$	-[c]		-[c]		1.63	4.86
$PO_3C_6H_9$	1.14	3.04	1.09	1.90	----	----
$P(OCH_2)_3CCH_3$	1.14	1.16	1.09	.547	1.63	3.48
$P(OC_2H_5)_3$	1.14	.940	1.09	.592	1.63	3.65
$P(C_6H_5)_3$	1.14	.130	1.09	0	1.63	0
$P(OC_6H_5)_3$	1.14	.057	----	----	----	----

[a] Rate constants determined in 1,2-dichloroethane at 47.9°C.

[b] Rate constants determined in chlorobenzene at 114.0°C.

[c] $P(n\text{-}C_4H_9)_3$ reacts with 1,2-dichloroethane.

initial rates at low ligand concentrations, and the molecular weight of $W(CO)_4$(dipy) in a solution containing a known amount of $PO_3C_6H_9$.

The solubility of $Mo(CO)_4$(dipy) in 1,2-dichloroethane was determined spectrophotometrically and was found to be 0.00935 mole/l, at 25°. This solubility increased only very slightly upon the addition of ligand to the 1,2-dichloroethane solutions. For ligand concentrations between 0.006 and 0.10 M, the solubility increased by about 1.5 to 4% for the three ligands used in the study. This small increase in solubility suggests that there is very little if any association between the complex and the ligand.

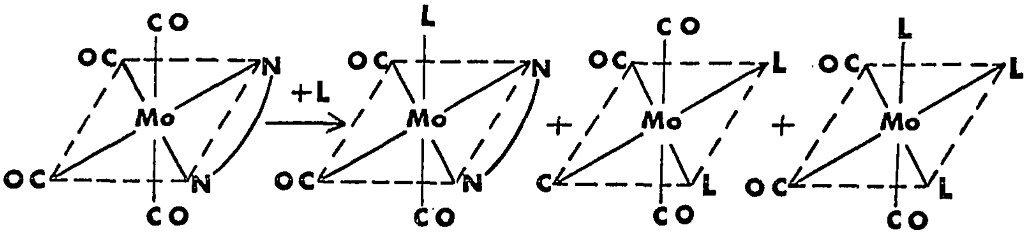
Initial rate constants for the reaction of $Mo(CO)_4$(dipy) with ligand concentrations of 0.004 to 0.02 M were determined at 47.9° (Table 9). At these low ligand concentrations the second term, $k_2[L][Mo(CO)_4(dipy)]$, in Equation 5 becomes very small and affects the reaction rate by less than 2%. Therefore Equation 5 essentially reduces to a first-order rate law. As shown by the data in Table 9, the rate constants determined at low [L] are very close to the previously determined first-order rate constants. Even at ligand concentrations which are less than the $Mo(CO)_4$(dipy) concentration, slight differences are still observed in the first-order rate constants. If association of the $Mo(CO)_4$(dipy) complex by excess ligand were responsible for the variations in k_1, it should be expected that k_1 for the different ligands should approach a common value at very low ligand concentrations. This, however, does not seem to be the case.

The molecular weight of a 1,2-dichloroethane solution containing known amounts of $W(CO)_4$(dipy) and $PO_3C_6H_9$ was determined by means of a vapor pressure osmometer. The molecular weight obtained for the solution of the ligand and the complex was within 1% of the value predicted if there was no association taking place.

The reason for the variations in the first-order rate constants is not known. Although the kinetic data, solubility studies, and molecular weight study seem to indicate that the variations in k_1 are not due to ligand-complex association, they do not offer any explanation for the observed phenomenon.

Ratio of products

During the course of the reaction of $Mo(CO)_4$(N-N), where N-N = 2,2'-dipyridyl and 1,2-diamino-2-methylpropane, more than one reaction product is formed (Equation 6). Infrared



(6)

spectra taken of the reaction products after several kinetic runs in which a different concentration of ligand was used showed that the amount of each product formed depended on the concentration of ligand used (Figure 7). In order to determine exactly what affect the ligand concentration had on the amount of each product formed during a particular reaction, the concentration of each product was determined as a function of the ligand concentration. This was done for both the $Mo(CO)_4(dipy)$ and $Mo(CO)_4(diamine)$ systems using $P(OCH_2)_3CCH_3$ as the entering ligand and 1,2-dichloroethane as the reaction solvent.

First of all, molar extinction coefficients were determined for the reactants and the products. They were found for $Mo(CO)_4(dipy)$, $Mo(CO)_4(diamine)$, $Mo(CO)_3(dipy)[P(OCH_2)_3CCH_3]$, $Mo(CO)_3(diamine)[P(OCH_2)_3CCH_3]$, $Mo(CO)_4[P(OCH_2)_3CCH_3]_2$, and $Mo(CO)_3[P(OCH_2)_3CCH_3]_3$ to be 1130, 1204, 1900, 2000, 1620, and 2630 l./cm. mole, respectively. The highest frequency C-O absorption of each complex was used, except for $Mo(CO)_3(dipy)[P(OCH_2)_3CCH_3]$ and $Mo(CO)_3(diamine)[P(OCH_2)_3CCH_3]$ for which the band at about 1855 $cm.^{-1}$ was used, for this determination.

In order to determine the amounts of each product formed, five runs were normally carried out at the same time. In each run the same concentration of the metal carbonyl complex was used while the ligand concentration was varied from about 0.1 M to about 1.0 M. The reactions were allowed to proceed until all of the starting $Mo(CO)_4(N\text{-}N)$ complex had completely reacted. After this time the infrared spectrum of each reaction solution was carefully recorded and the absorbance of each product band was measured. When the infrared spectra were recorded, the solution used in the solvent cell of the double-beam spectrophotometer contained the same concentration of ligand as was used in the reaction. This technique cancelled out all of the extraneous absorbances due to the ligand. From the absorbance of each product band and its molar extinction coefficient, the concentration of each product was determined using Beer's law. The results are shown in Table 16.

The two-term rate law shown in Equation 5 suggests that $Mo(CO)_4(N\text{-}N)$ reacts with L by two different and distinct mechanisms (14). Since in the $Cr(CO)_4(N\text{-}N)$ reactions the rate of reaction is first-order and the only product is cis-$Cr(CO)_3(N\text{-}N)L$, it can be reasonably assumed that the ligand-independent term of the two-term rate law for the reaction of $Mo(CO)_4(N\text{-}N)$ leads to the formation of only cis-$Mo(CO)_3(N\text{-}N)L$. The ligand dependent term which governs the second order mechanistic path therefore can lead to the formation of both cis-$Mo(CO)_3(N\text{-}N)L$ and cis-$Mo(CO)_4L_2$.

The ratio of the amounts of the products obtained from the two reaction paths must be proportional to the ratio of

Table 16. The concentration of products formed in the reaction of $Mo(CO)_4(N\text{-}N)$ with varying concentrations of $P(OCH_2)_3CCH_3$ in 1,2-dichloroethane

[L]	$[Mo(CO)_4L_2]$	$[Mo(CO)_3L_3]$	$[Mo(CO)_3(N\text{-}N)L]$	$\frac{[Mo(CO)_3(N\text{-}N)L]_2}{[Mo(CO)_4L_2]_2}$
		$Mo(CO)_4(dipy)$[a]		
0.943	0.00106	0.00067	0.00160	0.95
0.717	0.00095	0.00075	0.00172	1.03
0.470	0.00078	0.00062	0.00199	0.97
0.235	0.00046	0.00046	0.00253	1.08
0.117	0.00027	0.00031	0.00284	1.22
		$Mo(CO)_4$(1,2-diamino-2-methylpropane)[b]		
0.900	0.00125	0.00062	0.00009	0.38
0.600	0.00133	0.00061	0.00015	0.41
0.300	0.00126	0.00063	0.00027	0.48
0.210	0.00120	0.00068	0.00038	0.45
0.120	0.000968 ±	0.00053	0.00059	0.36
0.060	0.000747	0.00055	0.00087	0.39

[a] At 58.1°.

[b] At 47.9°.

the first-order rate constants describing the rate of formation of these products. Therefore

$$\frac{k_1}{k_2[L]} \cong \frac{[Mo(CO)_3(N\text{-}N)L]_1}{[Mo(CO)_4L_2]_2 + [Mo(CO)_3(N\text{-}N)L]_2}$$

In this equation the subscript 1 represents rate constant or product of first-order process, 2 represents rate constant or product of second-order process, 1,2 will represent the total product formed by both processes, and i will represent initial concentrations. All of the concentrations are in moles per liter. Since

$$[Mo(CO)_4(N\text{-}N)]_i = [products]$$

and

$$[products] = [Mo(CO)_4L_2]_2 + [Mo(CO)_3(N\text{-}N)L]_1 + [Mo(CO)_3(N\text{-}N)L]_2$$

then

$$[Mo(CO)_3(N\text{-}N)L]_1 = \frac{k_1[Mo(CO)_4(N\text{-}N)]_i}{k_1 + k_2[L]}$$

and

$$[Mo(CO)_3(N\text{-}N)L]_2 = [Mo(CO)_3(N\text{-}N)L]_{1,2} - [Mo(CO)_3(N\text{-}N)L]_1$$

The ratio of the amounts of the two products formed only by the second-order path is therefore

$$\frac{[Mo(CO)_3(N\text{-}N)L]_2}{[Mo(CO)_4[2]_2} = \frac{[Mo(CO)_3(N\text{-}N)L]_{1,2} - \dfrac{k_1[Mo(CO)_4(N\text{-}N)]_i}{k_1 + k_2[L]}}{[Mo(CO)_4L_2]_2}$$

The concentration of $[Mo(CO)_3(N\text{-}N)L]_{1,2}$ is taken as the sum of $[Mo(CO)_3(N\text{-}N)L]$ and $[Mo(CO)_3L_3]$ since $Mo(CO)_3(N\text{-}N)L$ is the initial product of the reaction, and $Mo(CO)_3L_3$ is formed by the further reaction of $Mo(CO)_3(N\text{-}N)L$ with excess

L. Since all of the terms in the above expression for the ratio of second-order product concentrations are known, it is a simple matter to calculate the ratio for different [L]. The values of this ratio calculated from experimental points are listed in Table 16. The fact that the relative concentrations of the second-order products is independent of the concentration of L used in the reaction firstly supports the assumptions as to what products are formed by each reaction path and secondly indicates that the initial intermediate formed in the second-order mechanism reacts to yield the two products by paths which do not depend on the concentration of L. These results will be discussed in relation to the possible mechanisms in the Discussion section.

Infrared Studies

In complexes of the type $M(CO)_4$(X-o-phen), any changes in the nature of X which alter the basicity of the substituted o-phenanthroline have a significant effect on the C-O stretching frequencies of the tetracarbonyl complex. The infrared frequencies listed in Table 17 bear this out. The data in Table 17 show that as X is changed so as to make the substituted o-phenanthroline more basic there is a fairly regular decrease in the C-O stretching frequencies of the complexes. Also given in Table 17 are the C-O stretching frequencies of two of the products of the reaction of

Table 17. C-O stretching frequencies (cm.$^{-1}$) of M(CO)$_4$ (X-*o*-phen) and Cr(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$](X-*o*-phen) complexes in CHCl$_3$

X-*o*-phen number	pK$_a$				
			Cr(CO)$_4$(X-o-phen)		
		(m)	(vs)	(s)	(s)
1	3.47	2010	1910.5	1889	1837
2	3.57	2010	1912	1891	1838
3	4.84	2007	1905	1881	1829
4	4.86	2008	1907	1883	1831
5	5.00	2007.5	1905	1881	1829
6	5.90	2006.5	1903	1878	1825
7	6.31	2006	1901	1874	1822
8	6.45	2006	1901	1874	1822
			Mo(CO)$_4$(X-o-phen)		
		(m)	(vs)	(s)	(s)
1	3.47	2016	1913	1885	1838
2	3.57	2016.5	1915.5	1888	1840
3	4.84	2013	1909	1879	1831
4	4.86	2014	1910	1881	1833
5	5.00	2014	1909	1878	1829
6	5.90	2013	1906	1875	1826
7	6.31	2012	1905	1873	1824
8	6.45	2012	1905	1873	1824
			W(CO)$_4$(X-o-phen)		
		(m)	(vs)	(s)	(s)
2	3.57	2013	1907	1886	1840
4	4.86	2010	1901	1877	1831
7	6.31	2008	1895	1871	1822
		Cr(CO)$_3$[P(OCH$_2$)$_3$CCH$_3$](X-o-phen)			
		(s)	(s)	(s)	
3	4.84	1936	1845	1803	
7	6.31	1933	1839	1796	

$Cr(CO)_4$(X-o-phen) with $P(OCH_2)_3CCH_3$. They also show a similar trend in that there is a lowering of the C-O stretching frequencies with increasing pK_a of the X-o-phen.

The most significant deviations from a continuous decrease in the C-O strethcing frequencies with increasing pK_a of the X-o-phen are for the complexes $M(CO)_4$(5-nitro-o-phen). These complexes have higher C-O stretching frequencies than would be predicted for their pK_a value. These complexes also showed unexpectedly low values for the first-order rate constants, k_1, listed in Table 14. Since both the C-O stretching frequencies and k_1 are slightly inconsistent with the pK_a value, some doubt is cast on the correctness of the pK_a value.

Equilibrium Studies

The data obtained from the equilibrium study of the reaction of complexes of the type $M(CO)_4$(X-o-phen), where M = Cr and Mo, with a number of ligands are listed in Tables 18 and 19. For the case where the metal was chromium, the equilibrium constants were very reproducible. The accuracy for these constants are probably within ±10%. For the molybdenum complexes, the reporducibility was a little poorer, normally about ±15%. The enthalpies and entropies listed in Table 20 were calculated from the equilibrium constants determined at two different temperatures.

Table 18. Equilibrium constants for the reaction of $M(CO)_4(N\text{-}N)$ with L at 45° in $\underline{o}$-dichlorobenzene

Ligand L	[L]	10^3[CO]	$10^3[M(CO)_4(N\text{-}N)]$	$10^3[M(CO)_3(N\text{-}N)L]$	K_{eq}
			$Cr(CO)_4(\underline{o}\text{-phen})$		
$P(\underline{n}\text{-}C_4H_9)$	0.0165	4.32	3.97	2.89	0.19
	0.0164	4.32	3.87	3.05	0.20
$PO_3C_6H_9$	0.0035	4.20	4.12	8.71	2.4
	0.0062	4.27	3.60	6.03	1.2
$P(OCH_2)_3CCH_3$	0.0715	4.28	2.54	7.34	0.18
	0.128	4.30	1.55	10.10	0.22
	0.0219	4.21	5.47	5.70	0.20
$P(OC_4H_9)_3$	0.0230	4.28	3.65	3.53	0.17
	0.0114	4.28	3.97	1.93	0.18
$P(\underline{i}\text{-}OC_3H_7)_3$	0.0384	4.27	4.88	1.30	0.030
	0.0328	4.26	5.65	1.32	0.030
	0.0165	4.26	4.62	0.52	0.029
$P(OC_2H_5)_3$	0.241	4.23	1.75	9.27	0.092
	0.239	4.23	1.87	11.61	0.11
	0.0849	4.35	2.80	6.86	0.12
$P(OCH_3)$	0.0573	4.33	7.18	3.01	0.18
	0.0571	4.27	7.40	3.43	0.16
	0.0158	4.20	6.94	3.54	0.14
			$Cr(CO)_4(4,7\text{-diphenyl-}\underline{o}\text{-phen})$		
$P(\underline{n}\text{-}C_4H_9)_3$	0.0252	4.27	3.71	4.51	0.21
	0.00769	4.22	3.66	1.22	0.18
$P(OCH_2)_3CCH_3$	0.0628	4.25	1.73	4.64	0.18
	0.0168	4.26	4.14	3.38	0.21
	0.0514	4.26	1.89	4.70	0.21
$P(OC_4H_9)_3$	0.0217	4.23	3.90	3.98	0.20
	0.0219	4.23	3.68	3.76	0.20
	0.00654	4.25	4.01	1.17	0.19

Table 18 (Continued)

Ligand L	[L]	10^3[CO]	$10^3[M(CO)_4$ (N-N)]	$10^3[M(CO)_3$ (N-N)L]	K_{eq}
$P(i\text{-}OC_3H_7)_3$	0.0202	4.23	4.02	0.69	0.036
	0.0405	4.31	4.42	1.27	0.031
	0.0405	4.31	3.99	1.27	0.033
		$Cr(CO)_4$(3,4,7,8-tetramethyl-*o*-phen)			
$PO_3C_6H_9$	0.0540	4.24	1.73	5.67	0.26
	0.0520	4.24	2.46	7.77	0.26
	0.0150	4.28	3.52	3.08	0.25
$P(OCH_2)_3CCH_3$	0.139	4.23	1.45	4.89	0.10
	0.138	4.23	1.98	6.29	0.098
$P(n\text{-}C_4H_9)_3$	0.0758	4.24	3.84	4.29	0.063
	0.0737	4.24	4.59	6.44	0.081
	0.178	4.23	2.94	7.71	0.063
	0.0175	4.23	3.79	1.08	0.069
$P(OC_4H_9)$	0.0775	4.19	3.84	4.63	0.065
	0.0774	4.19	3.84	4.67	0.066
	0.0286	4.26	3.23	1.30	0.060
	0.0143	4.26	4.00	0.78	0.059
$P(OC_2H_5)_3$	0.243	4.23	2.81	6.17	0.038
	0.242	4.23	3.14	6.89	0.038
	0.081	4.32	2.94	2.06	0.036
	0.421	4.32	3.35	1.01	0.035
$P(OC_6H_5)_3$	0.232	4.27	2.68	1.09	0.0075
	0.232	4.27	2.68	1.09	0.0075
			$Mo(CO)_4$(*o*-phen)		
$P(n\text{-}C_4H_9)_3$	0.0218	4.20	3.77	6.81	0.35
	0.0222	4.20	3.26	6.38	0.37
$P(OCH_2)_3CCH_3$	0.0299	4.28	3.10	5.25	0.25
	0.0227	4.33	4.37	4.88	0.21
	0.0318	4.31	1.56	3.29	0.28
$P(OC_4H_9)_3$	0.0506	4.18	2.54	6.07	0.20
	0.0499	4.18	2.87	6.79	0.20
	0.0126	4.20	3.08	4.44	0.48

Table 18 (Continued)

Ligand L	[L]	10^3[CO]	10^3[M(CO)$_4$ (N-N)]	10^3[M(CO)$_3$ (N-N)L]	K_{eq}
P($\underline{i}$-OC$_3$H$_7$)$_3$	0.0360	4.25	4.35	3.66	0.10
	0.0359	4.27	3.10	3.81	0.15
	0.0345	4.22	3.48	2.36	0.085
P(OC$_2$H$_5$)$_3$	0.242	4.22	0.757	8.32	0.19
	0.249	4.22	0.904	13.23	0.22
	0.0836	4.35	2.54	8.23	0.17
P(OCH$_3$)$_3$	0.0552	4.24	2.35	9.29	0.31
	0.0539	4.24	3.00	10.61	0.28
	0.0147	4.20	3.22	4.59	0.41
			Mo(CO)$_4$(4,7-diphenyl-$\underline{o}$-phen)		
P($\underline{n}$-C$_4$H$_9$)$_3$	0.0089	4.25	2.64	4.52	0.85
	0.0250	4.22	2.13	1.52	1.2
	0.0244	4.27	1.61	5.29	0.58
P(OCH$_2$)$_3$CCH$_3$	0.0629	4.25	1.20	4.46	0.25
	0.0525	4.27	1.55	4.29	0.23
	0.0139	4.27	2.69	3.18	0.36
P(OC$_4$H$_9$)$_3$	0.0226	4.18	1.40	3.07	0.41
	0.0213	4.18	2.68	4.57	0.34
	0.00567	4.25	2.99	2.04	0.51
P($\underline{i}$-OC$_3$H$_7$)$_3$	0.0350	4.22	2.06	1.88	0.11
	0.0350	4.22	2.07	1.91	0.11
	0.0196	4.23	3.65	1.33	0.077
			Mo(CO)$_4$(3,5,6,8-tetramethyl-$\underline{o}$-phen)		
P(OCH$_2$)$_3$CCH$_3$	0.0288	4.26	2.16	4.46	0.31
	0.264	4.23	1.94	3.90	0.32
			Mo(CO)$_4$(3,4,7-trimethyl-$\underline{o}$-phen)		
P(OCH$_2$)$_3$CCH$_3$	0.0234	4.24	4.28	4.35	0.18
	0.0463	4.24	5.06	9.01	0.16

Table 18 (Continued)

Ligand L	[L]	10^3[CO]	$10^3[M(CO)_4$ (N-N)]	$10^3[M(CO)_3$ (N-N)L]	K_{eq}
$P(OCH_2)_3CCH_3$	0.0249	4.24	4.17	2.71	0.12
	0.127	4.23	2.94	11.20	0.13
			$Mo(CO)_4$(3,4,7,8-tetramethyl-o-phen)		
$P(OCH_2)_3CCH_3$	0.0294	4.26	2.56	3.82	0.21
	0.0728	4.23	2.27	6.00	0.15
	0.0260	4.23	3.38	3.97	0.19
			$Mo(CO)_4$(3,4,6,7-tetramethyl-o-phen)		
$P(OCH_2)_3CCH_3$	0.0257	4.27	1.54	4.26	0.46

Table 19. Equilibrium constants for the reaction of $M(CO)_4$ (N-N) with L at 60° in o-dichlorobenzene

Ligand L	[L]	10^3[CO]	$10^3[M(CO)_4$ (N-N)]	$10^3[M(CO)_3$ (N-N)L]	k_{eq}
			$Cr(CO)_4$(o-phen)		
$P(n\text{-}C_4H_9)_3$	0.0496	4.32	4.55	9.57	0.18
	0.0521	4.32	3.76	7.07	0.18
$P(OC_4H_9)_3$	0.0229	4.38	5.32	5.37	0.19
	0.0231	4.38	5.15	5.16	0.19
$P(OCH_2)_3CCH_3$	0.0571	4.39	3.45	8.48	0.19
	0.0586	4.39	2.83	7.05	0.19
$P(i\text{-}OC_3H_7)_3$	0.305	4.39	3.90	8.01	0.029
	0.306	4.38	3.54	6.98	0.028
			$Cr(CO)_4$(3,4,7,8-tetramethyl-o-phen)		
$P(OC_4H_9)_3$	0.0253	4.35	5.68	3.04	0.092
	0.0252	4.35	5.65	3.08	0.092

Table 19 (Continued)

Ligand L	[L]	10^3[CO]	10^3[M(CO)$_4$ (N-N)]	10^3[M(CO)$_3$ (N-N)L]	K_{eq}
			$Mo(CO)_4$(*o*-phen)		
$P(C_4H_9)_3$	0.0480	4.36	1.15	10.97	0.88
	0.0112	4.33	3.84	6.47	0.65
$P(OC_4H_9)_3$	0.0285	4.36	1.69	9.05	0.82
	0.0125	4.37	2.78	6.29	0.79
	0.0117	4.37	3.50	7.03	0.75
$P(OCH_2)_3CCH_3$	0.0252	4.37	3.99	7.59	0.33
	0.0563	4.38	1.70	9.33	0.42
	0.0135	4.36	5.98	7.62	0.41
	0.0151	4.36	5.49	5.79	0.31
P(*i*-OC$_3$H$_7$)$_3$	0.127	4.38	0.984	6.62	0.23
	0.0586	4.36	3.46	8.87	0.19
			$Mo(CO)_4$(3,5,8-trimethyl-*o*-phen)		
$P(OCH_2)_3CCH_3$	0.0691	4.30	1.57	5.92	0.23
	0.0689	4.30	1.56	5.94	0.23
			$Mo(CO)_4$(3,4,7,8-tetramethyl-*o*-phen)		
$P(OCH_2)_3CCH_3$	0.0181	4.41	3.82	3.05	0.51
	0.0181	4.41	3.84	2.94	0.57

Table 20. Entropies and enthalpies obtained from equilibrium constants for the reaction of $Mo(CO)_4$(X-o-phen) with various ligands in o-dichlorobenzene

X-o-phen	ligand	pK_a	ΔH kcal./mole	ΔS e.u.
o-phen	$P(OCH_2)_3CCH_3$	4.86	5.6	14.9
3,5,8-trimethyl-o-phen	$P(OCH_2)_3CCH_3$	5.27	2.7	22.9
3,4,7,8-tetramethyl-o-phen	$P(OCH_2)_3CCH_3$	6.31	1.9	44.7
o-phen	$P(n\text{-}C_4H_9)_3$		1.2	31.6
o-phen	$P(OC_4H_9)_3$		2.1	41.8
o-phen	$P(OCH(CH_3)_2)_3$		8.8	23.4

DISCUSSION

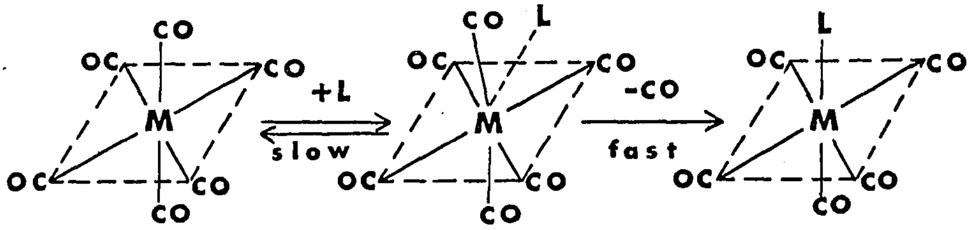
Reaction Kinetics and Mechanisms

The Group VI metal hexacarbonyls react with phosphine and phosphite ligands at a rate which is governed by a two-term rate law (Equation 3). This two-term rate law indicates that the reaction occurs by two mechanisms. The first term, $k_1[M(CO)_6]$, which depends only on the concentration of $M(CO)_6$, suggests a simple dissociative (S_N1) mechanism which probably proceeds through a five coordinated reaction intermediate (Equation 7).

$$M(CO)_6 \xrightarrow[\text{slow}]{-CO} M(CO)_5 \xrightarrow[\text{fast}]{+L} M(CO)_5L \qquad (7)$$

The positive values of $\Delta S_1^{\ddagger}$ in Table 5 support this type of mechanism. The enthalpies of activation for the first order path listed in Table 5 are within experimental error of the values of the activation energies obtained by other workers for the rate of exchange of ^{14}CO with the Group VI metal hexacarbonyls (18, 47) in the gas phase (Table 5). Since the ^{14}CO exchange most likely takes place by a dissociative mechanism, the good agreement in the values of activation energies for the first order paths suggest that the hexacarbonyls probably react with ligands in solution by a similar dissociative mechanism. That the reactions at least in part should follow a dissociative mechanism is not surprising since octahedral complexes are usually found to proceed by such a reaction path (10).

The second term of the two-term rate law, $k_2[L][M(CO)_6]$, is most unusual for an octahedral complex because it involves the concentration of L (50). The most probable mechanism which best explains this part of the rate law involves a nucleophilic attack by the ligand upon the metal forming a seven-coordinated intermediate or transition state which in turn yields the reaction product (Equation 8).



(8)

This type of S_N2 reaction mechanism is supported by negative values of $\Delta S_2^{\ddagger}$ listed in Table 5 (13).

Even though an S_N2 mechanism is the most probable, a number of reasons (50) have been given for not expecting octahedral complexes to react by a displacement mechanism. These reasons involve factors ranging from steric repulsions resulting from an expanded coordination shell to electrostatic repulsions between the metals filled d-orbitals and the attaching nucleophile. These factors probably account for the fact that only a very small number of octahedral complexes have been found to undergo reactions with nucleophiles at a rate which is dependent upon the concentration of the nucleophilic reagent (35, 50, 58, 61, 69). The Group VI metal hexacarbonyls offer the simplest and most straight forward case of a metal octahedral complex undergoing a nucleophilic attack by a nucleophile. Although the initial attack most probably occurs at the metal, a mechanism which involves an attack on one of the carbonyl carbons followed by a subsequent rearrangement cannot be ruled out.

If $M(CO)_6$ does undergo a true displacement reaction, the magnitude of the second order rate constant, k_2, should be a function of the steric and basic properties of the attacking nucleophile and the size of the central metal atom. The data in Table 4 indicates that this is indeed the case. As the attacking ligand is made more basic (decreasing value of Δ_{HNP}), the value of k_2 shows a corresponding increase. The values of k_2 for the reaction of $P(C_6H_5)_3$ and $P(OC_6H_5)_3$ with $Mo(CO)_6$ are not as different from each other as would be expected from their Δ_{HNP} values. Molecular models clearly show that $P(C_6H_5)_3$ is more sterically hindered from participating in a nucleophilic attack than is $P(OC_6H_5)_3$, and this probably accounts for the relatively low value of k_2 for $P(C_6H_5)_3$ as compared to $P(OC_6H_5)_3$.

The size of the central metal atom plays a large part in determining the magnitude of k_2. If a ratio of k_2/k_1

for $Cr(CO)_6$ (0.7), $Mo(CO)_6$ (9.6), and $W(CO)_6$ (34.8) are compared for the reaction with the same ligand, P(n-$C_4H_9)_3$, at the 112°, this can be readily seen. Since the values of k_1 and k_2 for a reaction carried out at a given ligand concentration will govern what fraction of the reaction will occur by each reaction path, the larger the value of k_2 with respect to k_1, the greater the percentage of the reaction that will proceed by the k_2 path. Since the magnitude of k_2 should be governed by the ease with which the complex can undergo a nucleophilic attack, the ratio of k_2/k_1 used here should give a qualitative measure of the importance of the nucleophilic attack path as compared to the CO dissociation path, and therefore, since these complexes are of the same type, give a qualitative measure of how steric hindrance within the octahedral complex will affect the ability of the complex to undergo this nucleophilic attack. Other effects however such as electronic effects can also appreciably alter the magnitude of k_1 and k_2 (12).

All of the complexes of the type $Cr(CO)_4$(N-N), where N-N = 2,2'-dipyridyl, 4,4'-dimethyl-2,2'-dipyridyl, 1,2-diamino-2-methylpropane, and X-o-phenanthroline, react with L at rates which are independent of the ligand concentration (Equation 4). The rate-determining step presumably involves the dissociation of a CO group from the tetracarbonyl complex to form a five coordinated reaction intermediate or transition state (Equation 9). One of the CO groups trans to each

$$Cr(CO)_4(N\text{-}N) \xrightarrow[slow]{-CO} Cr(CO)_3(N\text{-}N) \xrightarrow[fast]{+L} Cr(CO)_3(L)(N\text{-}N) \qquad (9)$$

other probably dissociates in these reactions since the product corresponds to the simple replacement of one of these CO groups. A C-O stretching frequency analysis (34) on some of these complexes suggests that the CO groups trans to each other are more weakly bonded to the chromium than the CO groups which are trans to the bidentate ligand. However no kinetic data are available to support this supposition.

The S_N1 mechanism for the $Cr(CO)_4(N\text{-}N)$ reactions is the same mechanism proposed to explain the ligand independent term of the two-term rate law for the $M(CO)_6$ reactions. Here as in the $M(CO)_6$ reactions an S_N1 mechanism is supported by the positive values of $\Delta S_1^{\ddagger}$ as shown by the data in Table 5. As expected for a first-order rate law, k_1 is independent of the nature of the entering nucleophile. However k_1 does depend greatly on the bidentate ligand present in the complex. The data listed in Table 14 for the reaction of $Cr(CO)_4$(X-o-phen) with $P(OCH_2)_3CCH_3$ point this out. As the basicity of the substituted o-phenanthroline in the $Cr(CO)_4$(X-o-phen) complex is increased, the first-order rate constant, k_1, also increases in value. The amount of the increase in k_1

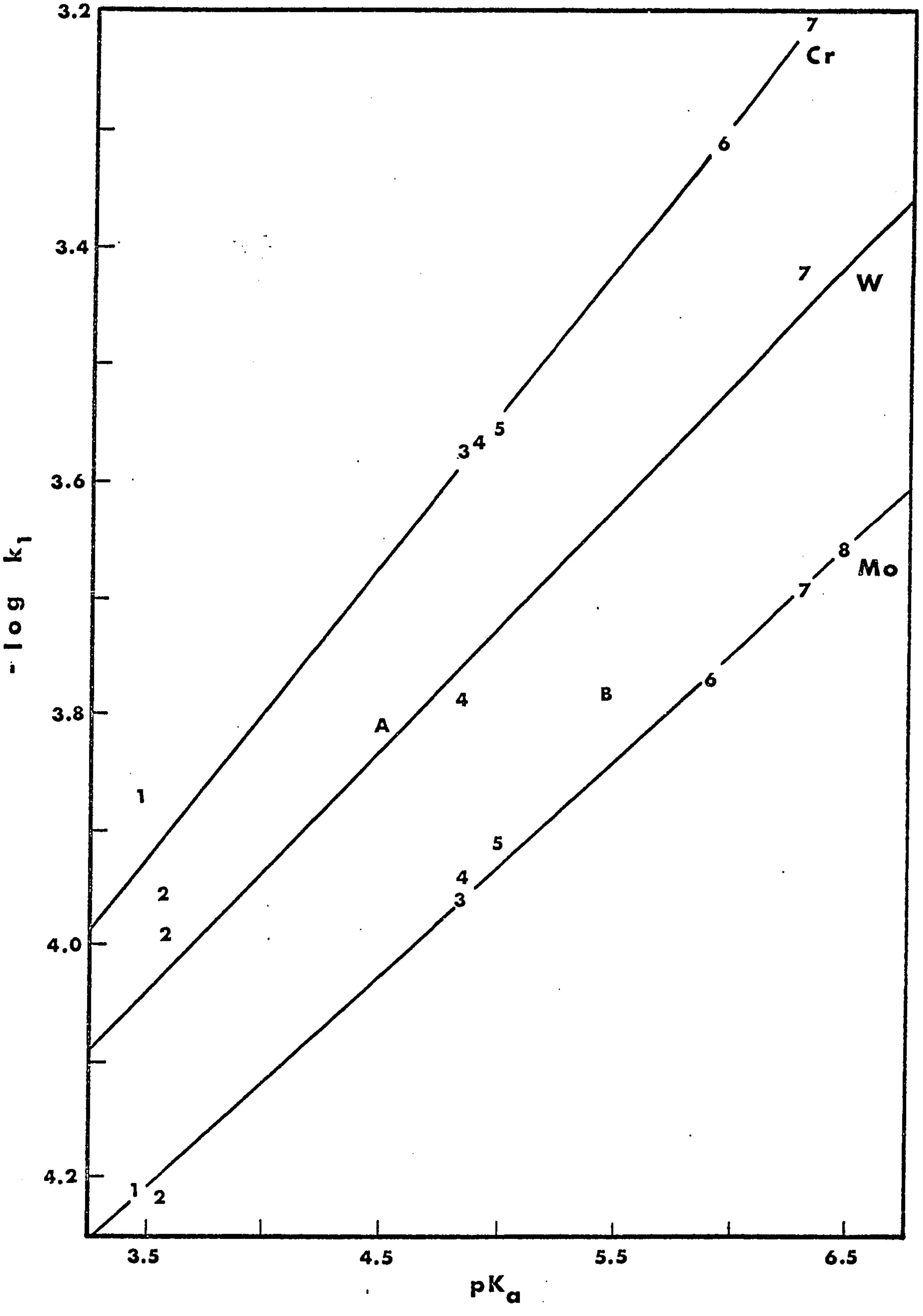
with the pK_a of X-o-phen is very regular and is quite predictable from the free energy plot shown in Figure 9. The slope of the line obtained from plotting log k_1 *vs.* pK_a is negative. This is consistent with a reaction mechanism which involves a decrease of electron density at the reaction center in the transition state (45, 68). Such a mechanism could be the simple S_N1 dissociative mechanism proposed for this reaction.

Since the first-order term for the reaction of $M(CO)_4(N\text{-}N)$ with L probably results from an S_N1 type dissociative mechanism, it might be expected that the first-order rate constant should show some solvent dependence. To see if this was the case the complexes $M(CO)_4(dipy)$, where M = Cr and Mo, were reacted with $P(OCH_2)_3CCH_3$ in four solvents of varying dielectric constants. The data in Table 21 show that the

Table 21. Rate constants for the reaction of $M(CO)_4(dipy)$ with $P(OCH_2)_3CCH_3$ in various solvents at 37.9°

		$Cr(CO)_4(dipy)$	$Mo(CO)_4(dipy)$	
Solvent	Dielectric constants	10^5k_1 sec.$^{-1}$	10^5k_1 sec.$^{-1}$	10^5k_2 l./mole sec.
Chlorobenzene	5.62	4.90	1.74	10.8
1,2-Dichloroethane	10.36	13.7	4.43	10.6
Acetone	20.7	17.6	5.30	9.67
Nitrobenzene	34.8	15.5	5.20	10.4

Figure 9. Free energy plots of $-\log k_1$ *vs.* pK_a for the reaction of $M(CO)_4$(X-*o*-phen) (where M = Cr, Mo, and W) with $P(OCH_2)_3CCH_3$. The numbers represent the X-*o*-phen as listed in Table 14. A and B represent the reactions of $Mo(CO)_4$(dipy) and $Mo(CO)_4$(4,4'-dimethyldipy) with $P(OCH_2)_3CCH_3$ in 1,2-dichloroethane at 47.9°

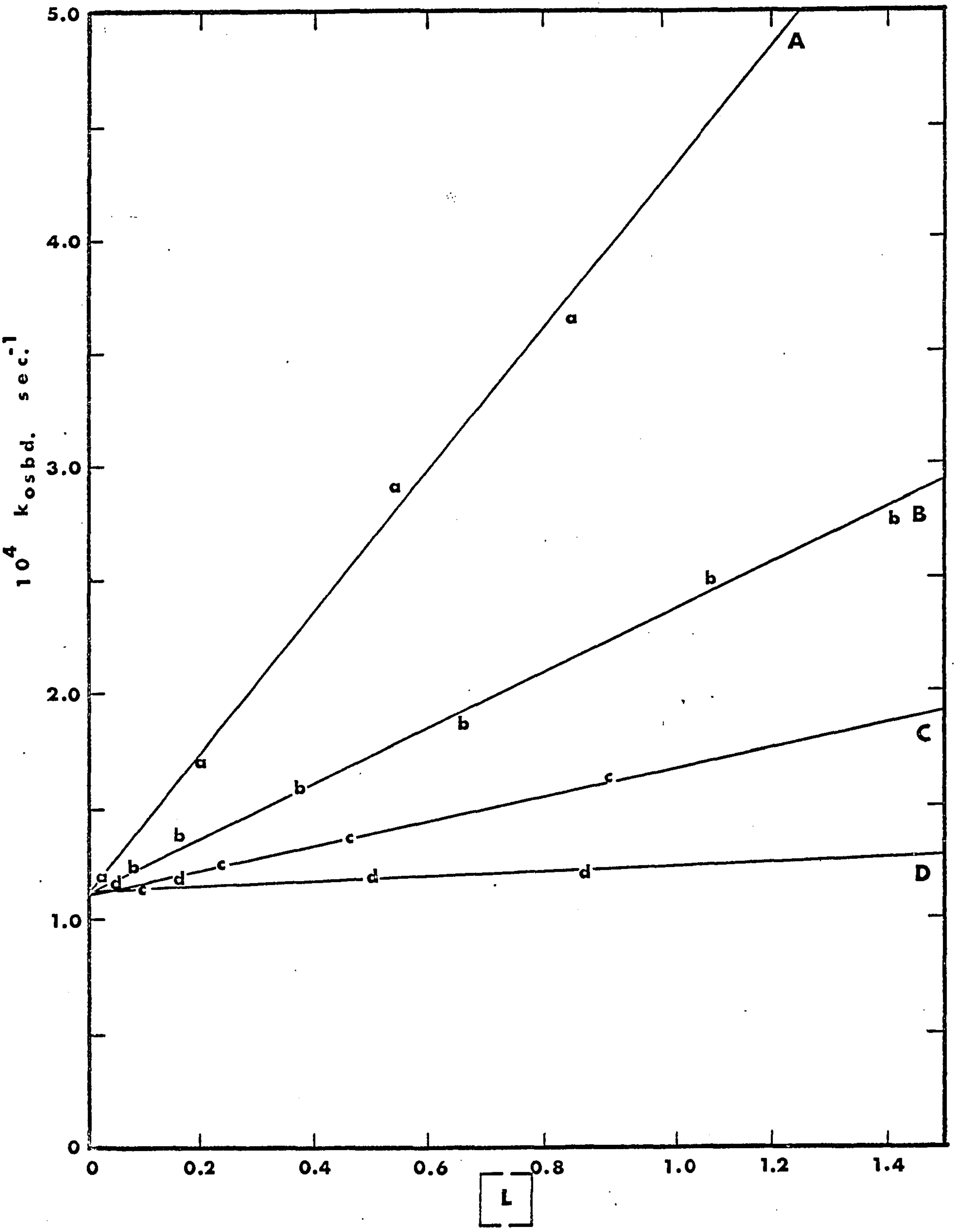

3.2
3.4
3.6
3.8
4.0
4.2
- log k_1
3.5
4.5
5.5
6.5
pK_a
Cr
W
Mo
1
2
2
1
2
3
4
5
6
7
7
A
4
B
3
4
5
6
7
8

rates are affected only to a small extent by the solvent. Similar small solvent effects have also been found in other carbonyl substitution reactions (3, 54, 60) and are probably to be expected for such non-ionic reactions even though the rate determining step involves a dissociative process.

If the metal in the $Cr(CO)_4(N\text{-}N)$ complexes is changed from Cr to Mo or W, the rate of reaction no longer follows a simple first order-rate law. A two-term rate law (Equation 5) similar to the one observed in the hexacarbonyl reactions is found. As pointed out before, this two-term rate law suggests that the reactions proceed by two different mechanisms. The first term, $k_1[M(CO)_4(N\text{-}N)]$, suggests a simple dissociative mechanism which is analogous to that observed for the reaction of $Cr(CO)_4(N\text{-}N)$ with phosphines and phosphites. The activation energies of about 25 kcal./mole and the positive or very slightly negative entropies of activation (Table 5) for the Mo and W reactions are very close to those obtained for the dissociative mechanism of $Cr(CO)_4(N\text{-}N)$ and support the same mechanism for the first-order portion of the $M(CO)_4(N\text{-}N)$reactions.

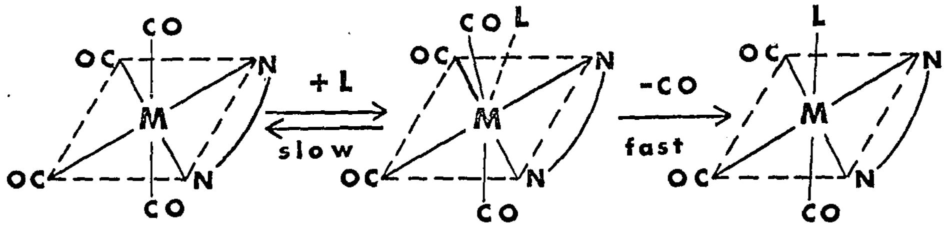
The magnitude of k_1 is again, as pointed out for the $Cr(CO)_4(N\text{-}N)$ reactions, a function of the bidentate ligand, N-N. Figure 9 shows a plot of log k_1 vs. pK_a for the reaction of $Mo(CO)_4$(X-o-phen) and $W(CO)_4$(X-o-phen) with $P(OCH_2)_3CCH_3$. The correlation is very good, and the slope

Figure 10. Plots of $k_{obsd.}$ vs. the concentration of L for the reaction of $Mo(CO)_4$(o-phen) with various phosphines and phosphites in 1,2-dichloroethane at 47.9°. A = $PO_3C_6H_9$, B = $P(OCH_2)_3CCH_3$, C = $P(OC_2H_5)_3$, and D = $P(OC_6H_5)_3$


$10^4\ k_{osbd.}\ sec.^{-1}$
5.0
4.0
3.0
2.0
1.0
0
0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
[L]
A
B
C
D
a
b
c
d

which is negative is consistent with an S_N1 mechanism. The magnitude of the slope is fairly small, $Cr(CO)_4$(X-o-phen) (-0.26) and $Mo(CO)_4$(X-o-phen) (-0.18), compared to most organic reactions which are known to undergo S_N1 mechanisms. Since in these reactions none of the species are charged, a small value for the slope would be predicted (68). However the values obtained here do compare favorably with the values obtained by Margerum and Steinhaus (42) for some reactions of $Ni(H_2O)_4(X\text{-}o\text{-phen})^{++}$ for which they proposed an S_N1 mechanism.

The second term of Equation 5, $k_2[M(CO)_4(N\text{-}N)][L]$, immediately suggests an S_N2 type displacement mechanism. This type of mechanism not only explains the ligand dependent reaction rates for the $Mo(CO)_4$(X-o-phen) reactions for which only one reaction product is formed (Equation 10), but it

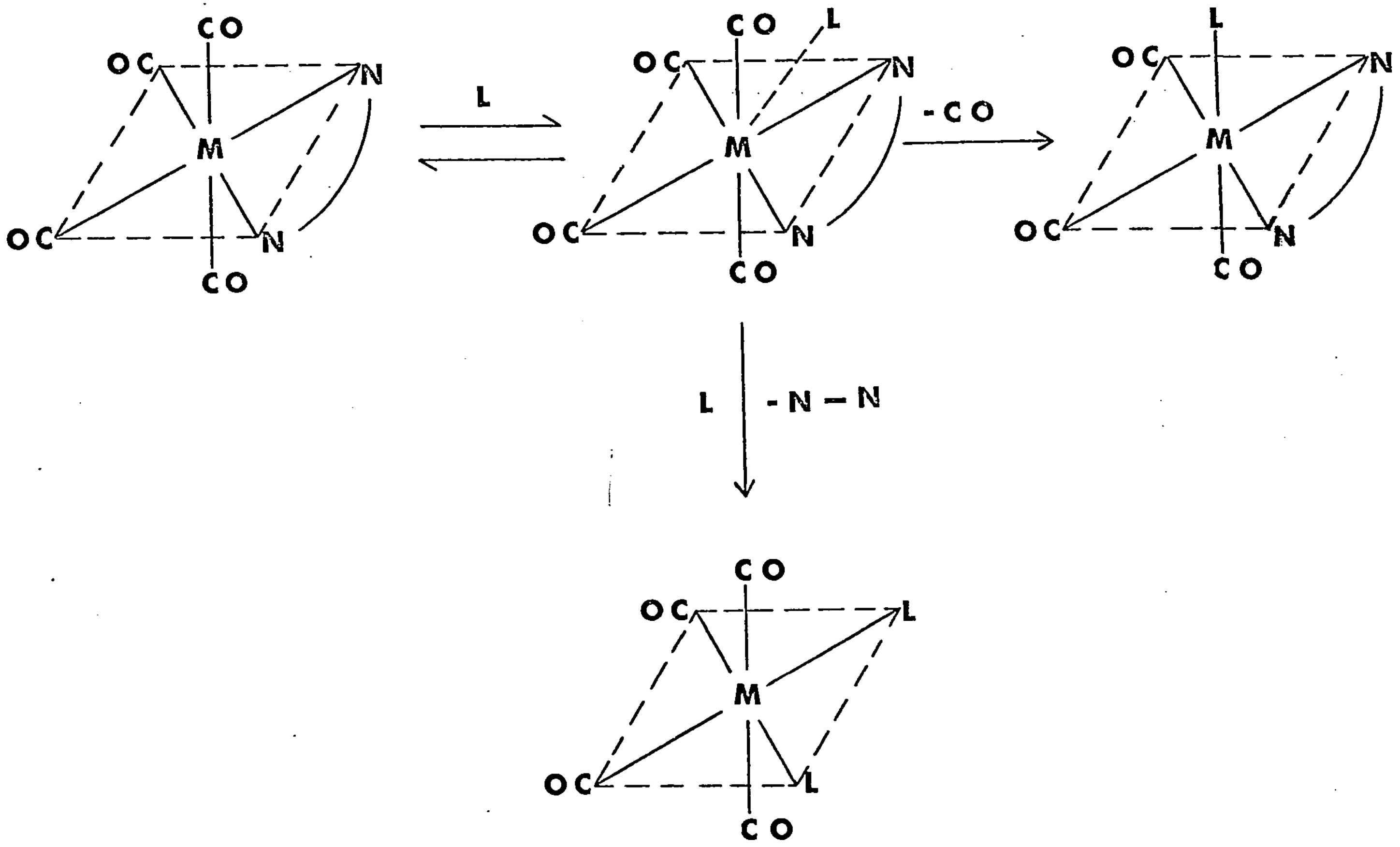


(10)

also explains the formation of more than one reaction product for N-N other than X-o-phen in amounts which are independent of the concentration of L used in the reaction (Scheme 1).

The displacement mechanism adequately accounts for all of the data. However, a special type of dissociation

Scheme I. Displacement mechanism for the reaction of $M(CO)_4(N\text{-}N)$ with L


CO
OC
N
M
OC
N
CO
L
CO
L
OC
N
M
OC
N
CO
-CO
L
OC
N
M
OC
N
CO
L
-N—N
CO
OC
L
M
OC
L
CO

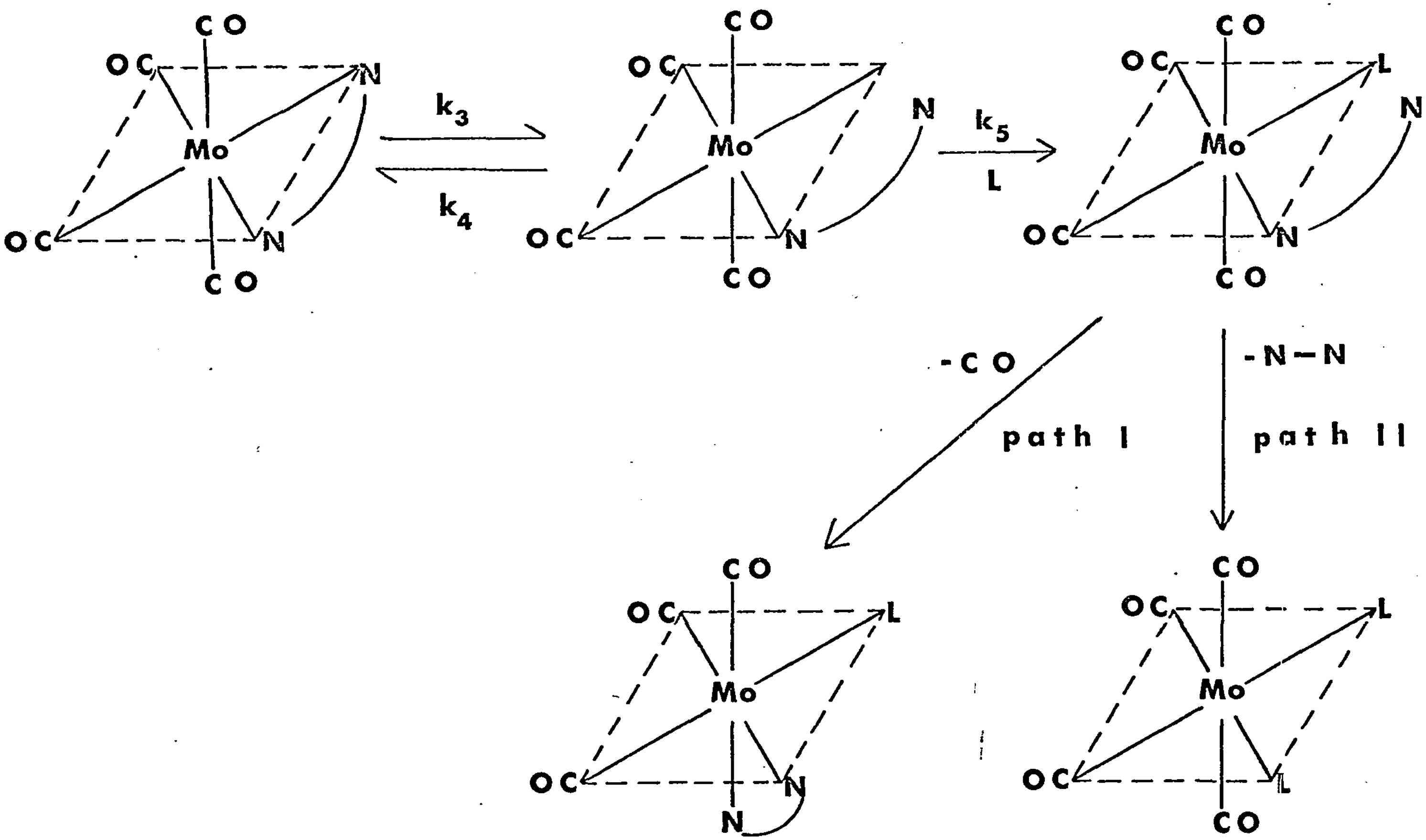
mechanism (Scheme II) will also explain the kinetic data. A steady-state treatment for the reaction of $M(CO)_4(N-N)$ by the mechanism shown in Scheme II yields the following rate expression. In this expression when $k_4 >> k_5$ [L] the

$$\text{Rate} = \frac{k_3k_5[M(CO)_4(N-N)[L]}{k_4 + k_5[L]}$$

equation reduces to a second-order rate law. Since it is likely that k_4 is much larger than $k_5[L]$, this mechanism offers another possible interpretation of the observed rate law. The rate expression predicts that at high concentrations of L, i.e., when $k_5[L] >> k_4$, the rate law should reduce to a first-order equation. Even at concentrations of L as high as 1.7 *M*, the reaction rate shows no decrease in its dependence on L. Since the rates of paths 1 and 11 would very likely be independent of [L], the relative amounts of the two products would be independent of [L] in this mechanism also.

The dissociative mechanism shown in Scheme II may be of considerable merit for a bidentate ligand such as 1,2-diamino-2-methylpropane or 2,2'-dipyridyl which have non-rigid structures and may be capable of forming the proposed dissociated intermediate. o-Phenanthroline however has a rigid structure with the donor nitrogen atoms held rigidly in the same plane. A molecular model of the o-phenanthroline

Scheme II. Dissociative mechanism for the reaction of $M(CO)_4(N\text{-}N)$ with L


Mo
CO
OC
N
L
k_3
k_4
k_5
L
-CO
path I
-N—N
path II

complex clearly indicates that a dissociative mechanism of this type is not reasonable. That the o-phenanthroline complexes do not react by a mechanism involving o-phen dissociation is supported by the fact that $M(CO)_4L_2$ is not formed as one of the reaction products. For 2,2'-dipyridyl and 1,2-diamino-2-methylpropane complexes some of the $M(CO)_4L_2$ product is formed. However, since $M(CO)_4$(X-o-phen) probably does not react by a dissociative mechanism and yet still shows second-order kinetics, considerable support is given for a displacement mechanism for all of the $M(CO)_4$(N-N) complexes. Also since a dissociative mechanism to account for the second-order character of the $M(CO)_6$ reactions is not plausible, more support is given for a displacement mechanism here.

The magnitude of the second-order rate constant, k_2, for the $M(CO)_4$(N-N) reactions, if it is in reality a result of a nucleophilic attack, should be sensitive to such factors as changes in steric properties of the octahedral complex, bidentate ligand, and attacking nucleophile, changes in the size of the central metal atom, changes in the base strength of the nucleophilic reagent, and changes in the electron density on the metal. These factors have been observed to be followed for all of the complexes studied.

Since the metal hexacarbonyls should be more susceptible to a nucleophilic attack than the sterically more demanding complexes of the type $M(CO)_4$(N-N), a greater percentage of their reaction should occur by a displacement mechanism than for the corresponding substituted complexes. Furthermore the susceptibility of the substituted complexes to a nucleophilic attack should decrease with increasing steric and electrostatic hindrance of the bidentate ligand. If the ratios of k_2/k_1 for $Mo(CO)_6$ (>50)* > $Mo(CO)_4$(diamine) (11.9) > $Mo(CO)_4$(dipy) (2.4) > $Mo(CO)_4$(o-phen) (1.0) > $Mo(CO)_4$(4,7-diphenyl-o-phen) (0.5) are compared for the reaction with the same ligand, $P(OCH_2)_3CCH_3$, at 47.9°C, this seems to be the case as this is the expected order of increasing electrostatic and steric hindrance to a nucleophilic attack.

The effect of steric hindrance of the bidentate ligand on the value of k_2 can be most readily seen for complexes of the same type if the second-order rate constants for the reaction of o-phenanthroline and 4,7-diphenyl-o-phenanthroline complexes of Mo with various phosphines and phosphites are compared (Table 15). Both of these bidentate ligands have approximately the same pK_a values and thereby approximately the same first-order rate constants. Since the electron density around the Mo atom for both of these complexes should be essentially the same, any deviations in the k_2 values should be due only to an increase in the amount of electrostatic and steric hindrance. Table 15 shows k_2 does

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*Estimated from activation parameters for reaction with $P(n\text{-}C_4H_9)_3$.

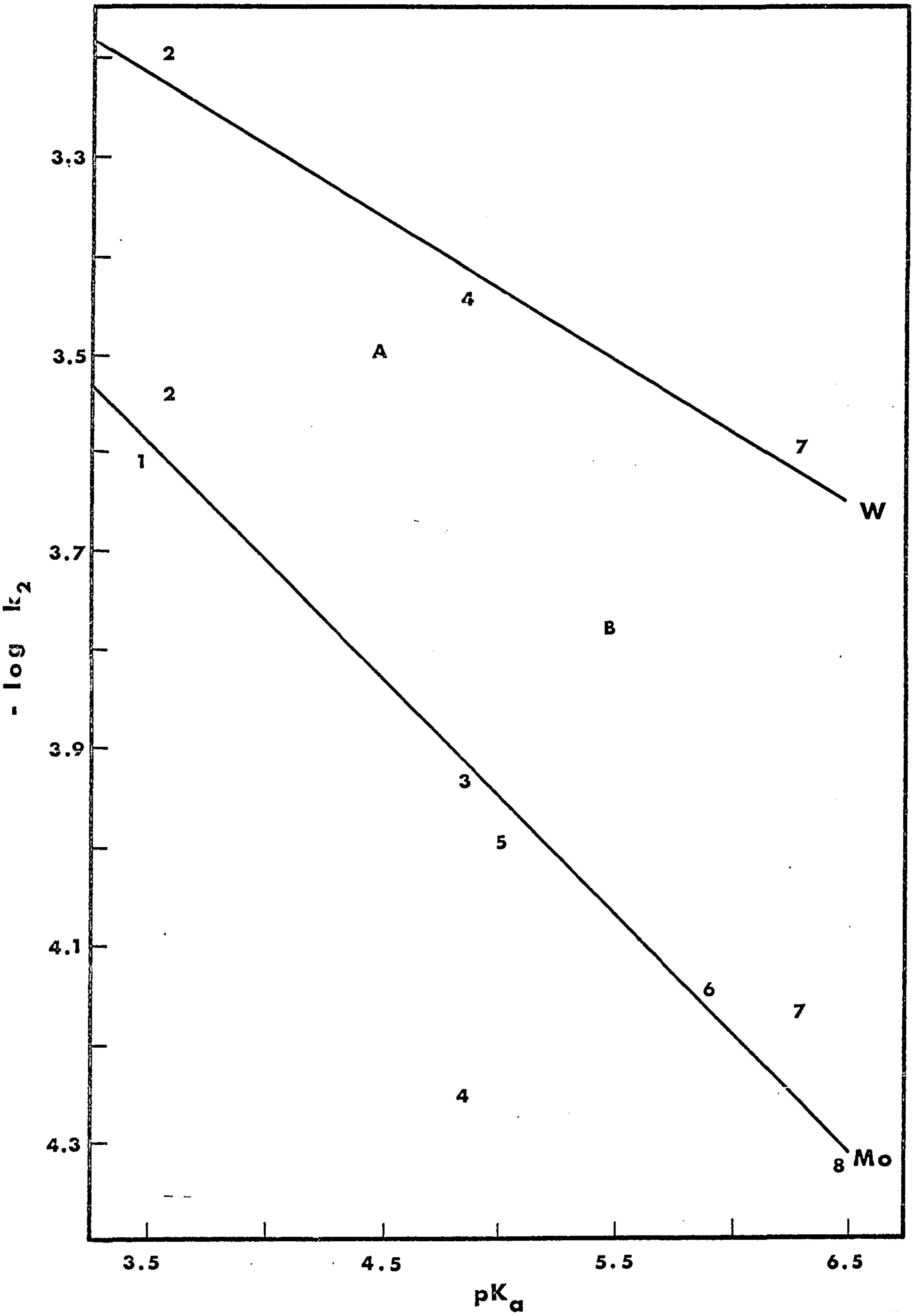
decrease substantially in going from o-phen to 4,7-diphenyl-o-phen for all of the ligands studied.

The size of the central metal atom is of considerable importance in determining the value of k_2. For the Group VI metals, the smallest atom, Cr, shows no k_2 term in its rate law for complexes of the type $Cr(CO)_4(N\text{-}N)$. The reaction rate of $Cr(CO)_6$, although it does follow a two-term rate law, dependence on the concentration of L is very small. The relative importance of k_2 over k_1 for the Group VI metal hexacarbonyls increases in going from Cr to Mo to W as was shown earlier. A similar trend in k_2/k_1 is obtained for the Cr, Mo, and $W(CO)_4$(o-phen) reactions with $P(OCH_2)_3CCH_3$ at 47.9°C. For these reactions values of k_2/k_1 are Cr (0.0), Mo (1.0), and W (9.5).

The basicity of the attacking ligand also plays an important role in the magnitude of k_2 as can be assessed from the data in Table 15. The exact effect of the ligand basicity on k_2 however is difficult to ascertain because all too often steric hindrance caused by the geometry of the ligand greatly complicates the interpretation. In general, k_2 decreases with L in the following order: $P(n\text{-}C_4H_9)_3 > PO_3C_6H_9 > P(OCH_2)_3CCH_3 \sim P(OC_2H_5)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3 > As(C_6H_5)_3$. This is the same trend in second-order rate constants as was observed by Basolo, et al., (54, 60) in the reaction of Rh and Co carbonyl complexes with a number of different nucleophilic reagents. This trend also follows the basicity of attacking ligand fairly well (24, 30, 59, 62).

A change in the electron density on the metal changes considerably the value of the second-order rate constant, k_2. This is clearly pointed out by the kinetic data for the substituted o-phenanthroline complexes of Mo and W which are listed in Table 14. These data show that when the pK_a of the o-phenanthroline is changed from a value of about 3.5 to 6.5, the value of k_2 decreases. This is expected since an increase in the basicity of the X-o-phen would increase the electron density on the metal thus making it less susceptible to a nucleophilic attack. The decrease in k_2 with increasing pK_a follows a linear free energy relationship surprisingly well (Figure 11). The only large deviation from the linear relationship is for 4,7-diphenyl-o-phenanthroline. The two phenyl groups of this bidentate ligand are very large and bulky compared to the other X substituents used in this study and steric hindrance probably accounts for its significantly lower value of k_2. The positive slope of the line obtained from the plot of log k_2 vs. pK_a is in itself consistent with a displacement mechanism in the reaction.

Figure 11. Free energy plots of -log k_2 vs. pK_a for the reaction of $Mo(CO)_4$(X-o-phen) and $W(CO)_4$(X-o-phen) with $P(OCH_2)_3CCH_3$. The numbers represent the X-o-phen in Table 14. A and B represent the reactions of $Mo(CO)_4$(dipy) and $Mo(CO)_4$(4,4'-dimethdipy) with $P(OCH_2)_3CCH_3$ in 1,2-dichloroethane at 47.9°



- log k_2
3.3
3.5
3.7
3.9
4.1
4.3
pK_a
3.5
4.5
5.5
6.5
2
4
7
W
A
2
1
B
3
5
6
7
4
8
Mo

CO Labilization

The main goal of this project was to determine whether or not certain CO groups were more labile in $M(CO)_4(N-N)$ type complexes than in the corresponding metal hexacarbonyls and if they were more labile to use the tools of chemical kinetics and infrared spectroscopy in an attempt to determine why.

Kinetic studies of the reaction of the Group VI metal hexacarbonyls with ligands definitely show that they are indeed kinetically quite inert. At temperatures near room temperature they undergo no ^{14}CO exchange (11) or substitution reactions with phosphines (41). They react with phosphines and phosphites at moderate rates only at temperatures of approximately 130° for $Cr(CO)_6$, 110° for $Mo(CO)_6$, and 150° for $W(CO)_6$. However if two CO groups in the metal hexacarbonyl are replaced by a bidentate nitrogen donor ligand, the Cr and Mo complexes react readily with phosphines and phosphites at temperatures only a little above room temperature and the W complexes react readily at about 100°C.

These observations are opposed to current theories about the bonding in these carbonyl complexes. Current bonding theory would predict that the replacement of two CO groups in the metal hexacarbonyl by a non-π-bonding nitrogen donor ligand should increase the amount of metal π-bonding to the remaining CO groups making them kinetically more inert than those in $M(CO)_6$. Since this is definitely not the case, an explanation was sought from kinetic and infrared data.

Kinetic studies by other workers have shown that not only do nitrogen donor ligands labilize CO groups in transition metal carbonyl complexes, but other groups do as well. On the basis of qualitative and quantitative substitution studies of $Mo(CO)_5X^-$ (X = Cl, Br, or I) (44), $Mo(CO)_5py$ (27), $Mn(CO)_5X$ (X = Cl, Br, or I) (3), $Mn(CO)_5H$ (16), $Mn(CO)_4(hfac)$, where hafc = hexafluoroacetylacetonate (38), and the complexes examined in this study (5, 7, 27, 28), it is apparent that CO groups in these complexes have been substantially labilized as a result of the introduction of the following ligands into the complex: Cl^-, Br^-, I^-, H^-, py, dipy, *o*-phen, hfac, and 1,2-diamino-2-methylpropane.

On the other hand from studies of the Group VI metal hexacarbonyls, $Mn(CO)_6^+$ (32), $Mo(CO)_5(CN\text{-}R)$ (19), $Cr(CO)_5PR_3$, $RO_2SMn(CO)_5$ (29), and $Mn(CO)_4(Br)L$, where L = phosphines, phosphites, and $As(C_6H_5)_3$ (4), it is clear that the following ligands do not significantly labilize the remaining CO groups when introduced into Cr(0), Mo(0), W(0), and Mn(I) octahedral complexes: CO, CN-R, RO_2S-, PR_3, $P(OR)_3$, and $As(C_6H_5)_3$. The donor atoms of the labilizing ligands are either first row elements or halogens. The non-labilizing ligands, however, exhibit second and third row element donor atoms with the exception of CO and CN-R. In general, the labilizing ligands would be classified as class a or "hard" bases and the non-labilizing ligands as class b or "soft" bases (2, 49).

Since certain ligands have the ability to labilize CO groups when introduced into octahedral complexes and other ligands actually make it more difficult to replace the CO groups when introduced into the same octahedral complexes, the answer as to why this is true must probably lie in the effect these ligands have on the reaction transition state and in their effect on the overall bonding in the octahedral complex.

Since the "hard" or labilizing ligands are in general non-π-bonding ligands, they would have the effect of making the central metal atom more negative during the transition state. This would be true because the labilizing ligands are not capable of participating in M-L π-bonding, and therefore would not be able to delocalize the increased electron density buildup on the metal which result from their σ-bonds. That the transition state is probably stabilized by introducing more electron density upon the metal was suggested by a temperature study of the reaction of two $Cr(CO)_4$(X-o-phen) complexes with $P(OCH_2)_3CCH_3$. In this study the following activation parameters were determined: for $Cr(CO)_4$(o-phen), $\Delta H^{\ddagger} = 26.4 \pm 0.8$ kcal./mole and $\Delta S^{\ddagger} = 7.0 \pm 2.6$ e.u.; for $Cr(CO)_4$(3,4,7,8-tetramethyl-o-phen) $\Delta H^{\ddagger} = 25.2 \pm 0.1$ kcal./mole and $\Delta S^{\ddagger} = 5.2 \pm 0.3$ e.u. The complex bearing the more basic o-phenanthroline has the lower enthalpy of activation, indicating probably a greater stabilization of the transition state than that which occurs for the o-phenanthroline of lesser basicity. Although the trends in the enthalpies observed here can definitely indicate a stabilization of the reaction transition state, this need not be the case. A weakening of the M-CO bond strengths in the $Cr(CO)_4$(X-o-phen) complex with increasing basicity of X-o-phen can also explain the decrease in the value of $\Delta H^{\ddagger}$.

Another example of the effect an increase in the "hardness" of the ligand has on the rate of CO dissociation can be seen in a study of the reaction of $Mn(CO)_5X$ (where X = Cl, Br, or I) with phosphine and phosphite ligands carried out by Angelici and Basolo (3). In this study the rate of CO dissociation from $Mn(CO)_5X$ was found to increase with X in the order: I < Br < Cl. This study shows that the degree of labilization does definitely increase with the "hardness" of the halide.

Therefore it can be stated with some degree of certainty that the "hard" or labilizing ligands have the ability to stabilize the transition state, and this can explain why CO groups are observed to be labilized when a "hard" base is introduced into these octahedral complexes. However this does not offer an explanation for the anomalous decreases in the C-O stretching frequencies with increasing basicity of the

X-*o*-phen as shown by the data in Table 17. Since a decrease in the C-O stretching frequency is normally associated with an increase in the amount of M-CO π-bonding, the question is raised as to why the CO groups are becoming increasingly labile when the C-O stretching frequencies indicate that the amount of M-C π-bonding is increasing. A possible answer to this question lies in the approximation of "symmetry factoribility" (26). According to this approximation the σ and π metallic orbitals in a octahedrally coordinated metal do not mix appreciably. Although S.F.A. Kettle (37) has shown that this approximation is probably not strictly valid for octahedral complexes having other than O_h point group symmetry, some workers have used it with considerable success (33, 51).

If there is no appreciable mixing of the σ and π metal orbitals, then the replacement of two "soft" CO groups in a metal hexacarbonyl by two "hard" nitrogen donor groups would result in a charge buildup on the metal. Since this increased electron density would be maintained almost entirely in the σ orbitals of the metal, the result would be a decrease in the M-CO σ-bond strength because of electrostatic repulsions between the more negative metal and the electron pair from the CO group. Furthermore the more basic the ligand, the greater should be the amount of labilization because the M-CO σ-bond should be correspondingly weaker.

To account for the observed changes in the C-O stretching frequencies with changing basicity of the bidentate ligand, it can be assumed that in these complexes there is some mixing of the σ and π orbitals, and therefore all of the electron density buildup on the metal is not maintained solely in the metal σ-orbitals, but some goes into the metal's π-orbitals as well. This would result in an increase in the amount of M-CO π-bonding as would be predicted from C-O stretching frequencies data. The amount of increase in M-CO π-bonding must however be considerably less than the amount of decrease in the M-CO σ-bond strength in order to explain the observed CO labilization. A "soft" ligand on the other hand would not labilize any CO groups because it has the π-acceptor orbitals available to prevent any appreciable charge buildup on the metal.

Since the rate and infrared studies seemed to indicate that the M-CO bond strength was probably being weakened when a "hard" base was introduced into the metals coordination sphere, an equilibrium study was conducted on the $M(CO)_4$(X-o-phen) system in an attempt to see if an increase in K_{eq} could be observed in going from the least basic to the most basic substituted o-phenanthroline. This might have been expected since the CO groups become more labile as the X-o-phen becomes more basic. The results of the equilibrium study show, however, that there is no trend in the equilibrium constants with change in the pK_a of the X-o-phen at a given temperature (Tables 18 and 19).

However the enthalpies and entropies listed in Table 20 show a very definite trend with a change in the basicity of the substituted o-phenanthroline. The values of the enthalpies decrease significantly as the X-o-phen is made more basic. This clearly indicates the reason why the CO groups in complexes of the type $M(CO)_4$(X-o-phen) are becoming more labile as the X-o-phen is made more basic is because the M-CO bond strength is decreasing. These results also suggest that the approximation of "symmetry factoribility" is probably valid for octahedral complexes having only C_{2V} point group symmetry, since this approximation does offer an explanation for the observed CO group labilization which is consistent with these equilibrium results as well as with all of the kinetic and infrared data collected in this study.

The enthalpies and entropies in Table 20 point out some other very interesting facts. First of all as might be expected, ΔH is a function of the basicity of the ligand used in the study. This is readily apparent if the ΔH value for $P(n\text{-}C_4H_9)_3$, the most basic ligand used in the study, is compared with the ΔH values for the other ligands listed in Table 20. Secondly, however, if the phosphites in Table 20 are compared, it can be seen that ligand basicity is not the only important factor in determining the value ΔH. Since all of these phosphites should have approximately the same basicities, the structure of the ligand must be of considerable importance in determining the size of ΔH. Of the three phosphites listed in Table 20, $P(OCH(CH_3)_2)_3$ has the largest positive value of ΔH. It is also the ligand which would be the most sterically hindered from bonding with the metal. Thirdly, the positive values of ΔH indicate that CO is a better coordinating ligand toward the zero valent Group VI transition metals than is a phosphine or a phosphite. Although this result is not surprising, it does indicate that the most important property of a ligand that determines how well it can coordinate with a zero valent Group VI element is the ligand's π-bonding ability.

The positive entropies in Table 20 are very surprising, because just looking at the overall equation for the reaction (Equation 11) it might be guessed that the entropies should

$$M(CO)_4(X\text{-}\underline{o}\text{-phen}) + L \rightleftharpoons M(CO)_3(X\text{-}\underline{o}\text{-phen})L + CO \tag{11}$$

be negative. The reason for this is that since L is much larger than CO, considerable entropy should be lost when it is coordinated into the complex and the CO group expelled. The positive entropies can be explained, however, if it is assumed that the ligand is highly solvated in the _o_-dichlorobenzene solvent and that the true equilibrium reaction is the one shown in Equation 12. That phosphine and phosphite

$$M(CO)_4(X\text{-}\underline{o}\text{-phen}) + L\cdot nSolvent \rightleftharpoons M(CO)_3(X\text{-}\underline{o}\text{-phen})L + CO + nSolvent \quad (12)$$

ligands interact fairly strongly with aromatic solvents has been demonstrated by Compton, Bertrand, and Verkade.* They found that the proton N.M.R. spectrum of $P(OCH_2)_3CCH_3$ changed markedly upon adding benzene and other aromatic solvents to a carbon tetrachloride solution of the phosphite. From a quantitative study of the shifts in the N.M.R. spectra with changing mole fraction of the aromatic solvent, they were able to calculate values of ΔH and ΔS for the ligand-solvent interactions. Although their ΔS values (<10 e.u.) are considerably smaller than the ΔS values determined here, their results do indicate that ligand-solvent interactions are important in determining the value of ΔS obtained from these equilibrium constants. It is not certain at this point whether this type of ligand-solvent interaction can explain the largeness of the ΔS values or not.

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*Results of R. D. Compton, R. D. Bertrand, and J. G. Verkade, submitted to Chem. Comm. for publication.

SUGGESTIONS FOR FUTURE WORK

Reaction Intermediates

Most octahedral complexes react with ligands at rates which are governed by a rate law which contains at least one term which is dependent only on the concentration of the complex. The most widely proposed mechanism used to explain this term when it appears in the rate law is a simple S_N1 dissociative mechanism which proceeds through a five coordinated reaction intermediate or transition state. However since these five coördinated species are so reactive under normal reaction conditions, their presence can not be detected and their existence can only be assumed.

The complexes of the type $M(CO)_4$(X-o-phen) offer an excellent opportunity to prove the existence of these five coordinated species and to study what factors govern their stabilities. The five coordinated species would have to be prepared in a very pure hydrocarbon glass at liquid nitrogen temperatures using ultraviolet irradiation. The preparations could be carried out in a specially designed low temperature I.R. cell which after preparation of the unstable intermediate could be heated to any desired temperature for temperature studies on the stabilities of the species.

$M(CO)_4(N-N)$ Reaction Product

During the reaction of $M(CO)_4(N-N)$ with L, one of the four CO groups is replaced by L to give cis-$M(CO)_3(N-N)L$ as the reaction product. It is not certain which CO group is being replaced by the entering ligand. One worker contends from a CO frequency analysis that it is probably the CO groups cis to the bidentate ligand that is being replaced. However, other workers using M.O. arguments contend it should be the CO groups trans to the bidentate ligand which should be the most easily replaced. An infrared study in which ^{14}CO is allowed to exchange with the $M(CO)_4(N-N)$ complex should very readily answer this question.

Equilibrium Studies

The equilibrium studies conducted in this study are quite incomplete and have only begun to scratch the surface of the vast amount of knowledge and insight about the bonding in metal carbonyl complexes that can be gained from this type of study. It should be expanded to include a large number of ligands and solvents and a whole variety of metal carbonyl complexes so that the many factors which govern the equilibrium constants, enthalpies and entropies can be better understood.

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VITA

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